

**Adsorption of Actinides onto Colloids as a Function of Time,  
Temperature, Ionic Strength, and Colloid Concentration**

**Waste Form Colloids Report for Yucca Mountain Program  
(Colloid Data Summary from 1999 to 2000 Research)**

**October 20, 2000**

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## Adsorption of Actinides onto Colloids as a Function of Time, Temperature, Ionic Strength, and Colloidal Concentration

### ABSTRACT

Plutonium, neptunium, uranium and americium are four radionuclides of concern for long-term emplacement of nuclear wastes at potential repository sites. These four actinides may have a high potential to migrate if attached to iron oxide, clay, or silica colloids in groundwater. Strong sorption of the actinides by colloids in groundwater may facilitate transport of these radionuclides along potential flowpaths. In porous media, colloids that are small in relation to the pores of the surrounding matrix may migrate long distances through the network of pore spaces.

Laboratory batch sorption experiments were conducted to evaluate: 1) sorption kinetics of plutonium-239 ( $^{239}\text{Pu}$ ), americium-243 ( $^{243}\text{Am}$ ), neptunium-237 ( $^{237}\text{Np}$ ), and uranium-238 ( $^{238}\text{U}$ ) onto colloids of hematite, montmorillonite, and silica in groundwater, 2) adsorption of these four actinides onto colloids as affected by ionic strength of the solutions, 3) adsorption of the four actinides onto colloids as a function of temperature, 4) adsorption of  $^{239}\text{Pu}$  and  $^{243}\text{Am}$  onto colloids as a function of colloid concentrations, and 5) desorption of the four actinides from actinide-loaded colloids as a function of time. Natural groundwater collected from Well J-13 at Yucca Mountain in Nevada (referred to as J-13 water) or synthetic groundwater (referred to as SYN.J-13 water) were used in all experiments. Our results show that the four actinides exhibit different adsorption/desorption behaviors in natural and synthetic groundwater. Adsorption of  $^{239}\text{Pu}$  and  $^{243}\text{Am}$  by colloids of hematite, montmorillonite, and silica was faster and greater than adsorption of  $^{237}\text{Np}$  and  $^{238}\text{U}$  in both natural and synthetic groundwater. Temperature did not significantly influence the adsorption of  $^{239}\text{Pu}$  and  $^{243}\text{Am}$  by hematite and silica colloids, but it did greatly increase the adsorption of  $^{239}\text{Pu}$  by montmorillonite colloids. Moreover, temperature also significantly influenced the adsorption of  $^{238}\text{U}$  and  $^{237}\text{Np}$  by all three types of colloids. While ionic strength did not significantly influence the adsorption of  $^{239}\text{Pu}$  and  $^{243}\text{Am}$  by hematite colloids, an increase in ionic strength decreased the adsorption of the four actinides by montmorillonite and silica colloids. Furthermore, uranium precipitation was observed in the solutions with ionic strength  $> 0.02\text{ M}$ . Adsorption of  $^{239}\text{Pu}$  and  $^{243}\text{Am}$  per unit mass of colloid was much higher at low colloid concentrations than at high colloid concentrations. The results from desorption experiments show that as much as 20%  $^{239}\text{Pu}$  was desorbed from silica and montmorillonite colloids, but less than 1%  $^{239}\text{Pu}$  was desorbed from hematite colloids over 293 days of desorption. Approximately 3% to 6% of  $^{243}\text{Am}$  were desorbed from hematite colloids, and as much as 40% of  $^{243}\text{Am}$  was desorbed from montmorillonite and silica colloids after 200 days of desorption. There was no evidence that  $^{237}\text{Np}$  and  $^{238}\text{U}$  desorbed from any of these three types of colloids in both natural and synthetic groundwater. Instead, adsorption of the residual activity in solution from the sorption phase of the experiments continued slowly during the 212 day desorption period.

*Key Words:*

*Plutonium-239/Neptunium-237/Uranium-238/Americium-243/Sorption kinetics/Desorption/  
Natural groundwater/Synthetic groundwater/Radionuclide-bearing colloids/Hematite  
colloids/Cheto Ca-montmorillonite colloids/Silica PST-1 colloids*

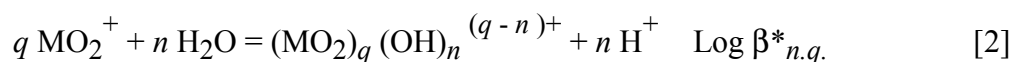
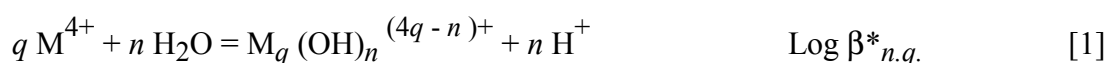
**INTRODUCTION**

Plutonium, neptunium, uranium, and americium are four radionuclides of concern for long-term emplacement of nuclear wastes. The environmental transport of Pu, Np, U and Am is governed by their solubility and speciation in groundwater, their tendency to be sorbed onto minerals, colloids and other matrices, and their propensity to form mobile species, such as dissolved cations, anions, and colloids. Formation of radionuclide-bearing colloids occurs by sorption of radionuclides onto colloids of iron oxide, clays, and silica in groundwater. We previously found that colloids of hematite, goethite, smectite, and silica rapidly sorbed soluble Pu(V) as well as colloidal Pu(IV) in groundwater (Lu *et al.*, 1998a and 1998b). Formation of Pu(IV) colloids was observed by chemical reduction of Pu(VI) in a 0.1 M HClO<sub>4</sub> solution (Knopp *et al.*, 1999). Triay *et al.* (1996) studied the generation and stability of colloids in Yucca Mountain groundwater and found that colloids of clays, silica, and iron oxides were generated in the groundwater and irreversible sorption of radionuclides onto these colloids occurred. Radio-colloids such as <sup>239</sup>Pu-, <sup>237</sup>Np-, <sup>243</sup>Am-, and <sup>247</sup>Cm-bearing colloids from high-level radioactive wastes, and <sup>137</sup>Cs-, <sup>90</sup>Sr-, and <sup>60</sup>Co-bearing colloids from low-level radioactive wastes can also be formed as waste package materials interact with groundwaters. Colloids can be mobilized by perturbations in the hydro-geochemistry of the aquifer system, particularly by waste disposal activity (Buddemeier, 1988; McCarthy and Degueldre, 1993).

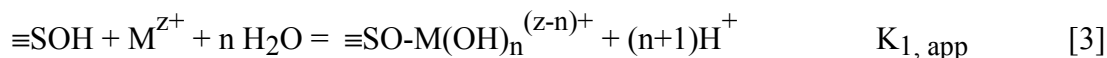
Groundwater colloids exist naturally in almost all subsurface environments and result from weathering of various geological formations. The chemical composition and concentration of colloids may differ from one groundwater to another, and from one geology to another (Degueldre *et al.*, 2000; Degueldre, 1997; Kim, 1991). According to McCarthy and Degueldre (1993), natural colloids range in size from 0.001  $\mu\text{m}$  to 1.0  $\mu\text{m}$  and in concentrations from 0.01 ppm to 100 ppm. The colloid concentration in groundwater is related to the stability of the colloids in the hydrochemical system. Colloid stability is a function of the chemical composition

of the water, as well as the status of the chemical and physical steady-state in the hydrogeochemical system (Degueldre *et al.*, 2000). Colloids generally have similar composition and surface characteristics to the immobile aquifer solids, but are mobile within aquifers. The large surface area of colloids ( $10^4$  to  $10^5$  m<sup>2</sup> kg<sup>-1</sup>) can offer significant sorption capacity for radionuclides; even for relatively low colloid mass concentrations in the aquifer (McCarthy and Degueldre, 1993; Vilks and Degueldre, 1991; Penrose *et al.*, 1990). Generally, the same processes that control adsorption of radionuclides to aquifer solids also affect their association with colloidal materials. Mobile colloids may enhance the transport of the strongly sorbing radionuclides along flowpaths and carry these radionuclides to the accessible environment. Champ, *et al.* (1982) observed that almost 75% of the Pu associated with colloidal particles were rapidly transported when groundwater was pumped through undisturbed aquifer cores. This observation was supported at the Nevada Test Site where transition metals and lanthanide radionuclides were shown to be associated with inorganic colloids in groundwater sampled 300 m from a nuclear detonation cavity (Buddemeier and Hunt, 1988). Furthermore, plutonium and americium were found to be associated with siliceous colloids in an alluvial aquifer at Los Alamos National Laboratory (Penrose, *et al.*, 1990). Uranium and its daughter species were also found associated with iron- and silica-rich colloids downgradient from a uranium deposit in Australia (Short, *et al.*, 1988).

Mineral oxides/hydroxides, especially those of Fe and Al in natural water systems, exhibit variably charged surfaces. The net surface charge changes with pH; being positive at low pH and negative at high pH. Sorption kinetics of dissolved metals on oxides and hydroxides depend on the type of surface and metal being studied, although they are generally rapid (Sparks, 1995). Surface complexation is the dominant mechanism for adsorption of actinide contaminants onto oxides or hydroxides in a solid/aqueous interface system (Fuger, 1992). This mechanism results in the formation of actinide-hydroxide complexes on the surface of iron oxide colloids. According to Fuger (1992), hydrolysis reactions of quadrivalent and pentavalent actinides can be described as follows:



Fuger (1992) and Sanchez, *et al.*, (1985) reported that the surface complexation of a soluble metal is correlated to the hydrolysis of the aqueous metal ion. Therefore, adsorption of actinides onto iron oxide can be chemically described as follows: (Liang and McCarthy, 1995):



where  $\equiv\text{SOH}$  denotes a surface site, and  $\equiv\text{SO-M}(\text{OH})_n^{(Z-n)+}$  is the complex on the surface of colloids.  $K_{1, \text{app}}$  is the apparent surface equilibrium constant and is defined as:

$$K_{1, \text{app}} = [\equiv\text{SO-M}(\text{OH})_n^{(Z-n)+}][\text{H}^+]^{(n+1)} / [\equiv\text{SOH}][\text{M}^{Z+}] \quad [4]$$

Thermodynamic calculations show that Pu(V) is in a stable oxidation state in the pH range of 5 to 7 at a pE of 12 and that Pu(VI) is the most stable oxidation state at higher pH values (Sanchez, *et al.*, 1985). It has been assumed that adsorption of Pu(IV) onto suspended particulate matter is due to the interaction of the strongly hydrolyzable Pu(IV) oxidation state with the surfaces of natural particulate matter (Sanchez, *et al.*, 1985). Keeney-Kennicutt and Morse (1985) found that  $\text{Pu(V)O}_2^+$  can be adsorbed onto goethite, aragonite, calcite and  $\delta\text{-MnO}_2$  in dilute solutions and seawater. The adsorption behavior of  $\text{Pu(V)O}_2^+$  is influenced by oxidation-reduction reactions occurring on the mineral surface. Keeney-Kennicutt and Morse (1985) also reported that adsorption of  $\text{Pu(V)O}_2^+$  on goethite results in a reaction in which Pu(IV) and Pu(VI) are formed on the mineral surface. Then, the Pu(VI) is slowly reduced to Pu(IV), leaving Pu(IV) as the dominant surface Pu species. Sanchez, *et al.* (1985) studied adsorption of soluble Pu(IV) and Pu(V) on goethite from a sodium nitrate solution and found that redox transformations are an important aspect of Pu adsorption chemistry. The adsorption behavior of Pu on goethite is related to the different hydrolytic characters of these two oxidation states in the solution. The adsorption of the more strongly hydrolyzable Pu(IV) occurred in the pH range 3 to 5, whereas adsorption of Pu(V) occurred at a pH range of 5 to 7 (Sanchez, *et al.*, 1985).

Unfortunately, information on affinity, kinetics, and reversibility of sorption, which is critical to evaluate the significance of colloids in relation to actinide transport, is largely

unavailable for groundwater colloids. There is also little information on the effect of temperature, ionic strength, and colloid concentrations on the adsorption of plutonium, neptunium, uranium, and americium by colloids of iron oxide, clays, and silica in groundwater. Desorption (reversibility) could be the result of several different mechanisms. For example, reduction of Fe(III) coated on clay particles would release occluded Pu into water. We previously found that removal of iron oxide from clay particles by a reducing reagent liberated large amounts of  $^{239}\text{Pu}$  into solution (Lu, *et al.*, 1998). Anoxic conditions may also result in dissolving the ferric oxyhydroxide coatings cementing clay particles to the aquifer solids (Ryan and Gschwend, 1990), which enhances the mobilization of clay colloids in groundwater [This is a colloid detachment mechanism, not a desorption mechanism.]

Laboratory batch sorption experiments were conducted to evaluate: 1) adsorption kinetics of  $^{239}\text{Pu}$ ,  $^{243}\text{Am}$ ,  $^{237}\text{Np}$ , and  $^{238}\text{U}$  onto colloids of hematite, montmorillonite, and silica in groundwater, 2) adsorption of these four actinides onto colloids as a function of temperature, 3) adsorption of the four actinides onto colloids as a function of solution ionic strength, 4) adsorption of  $^{239}\text{Pu}$  and  $^{243}\text{Am}$  onto colloids as a function of colloid concentrations, and 5) desorption of the four actinides from actinide-loaded colloids as a function of time. Natural groundwater collected from Well J-13 at Yucca Mountain in Nevada (referred to as J-13 water) or synthetic groundwater (referred to as SYN.J-13 water) were used in all of the experiments. Plutonium-239(V), neptunium-237(V), uranium-238(VI) and americium-243(III) were used as the radioisotopes in all experiments.

## EXPERIMENTAL PROCEDURE

### Waters

Natural groundwater (referred to as J-13 water) was collected in the fall of 1994 from the Well J-13 at Fortymile Wash, east of Yucca Mountain, Nevada. The water was filtered through a 0.05  $\mu\text{m}$  nylon filter membrane to eliminate natural colloids and microbes existing in the water. The composition of the filtered water was analyzed using a Varian Liberty 220 ICP (inductively coupled plasma) emission spectrometer and a Dionex DX 600 ion chromatograph system. The

alkalinity of the water was measured by a titration method (Rhoades, 1982). The natural groundwater had a pH of 8.21, an alkalinity of  $22.5 \text{ meq L}^{-1}$ , and an ionic strength of 0.005 M. It contained 1.0 ppm of total organic carbon, 13.3 ppm Ca, 46 ppm Na, 1.9 ppm Mg, 5.4 ppm K, 30.3 ppm of Si, 109 ppm  $\text{HCO}_3^-$ , 6.9 ppm  $\text{Cl}^-$ , 18.5 ppm  $\text{SO}_4^{2-}$ , and 1.5 ppm  $\text{NO}_3^-$ . It also contained small amounts of Al ( $< 0.1 \text{ ppm}$ ), Fe ( $< 0.01 \text{ ppm}$ ) and Mn ( $< 0.01 \text{ ppm}$ ).

The synthetic groundwater was prepared by dissolving 2.8 mg of sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) and 192 mg of sodium bicarbonate ( $\text{NaHCO}_3$ ) per liter of nanopure deionized water, which was previously filtered through a  $0.05 \mu\text{m}$  nylon filter membrane. The synthetic groundwater, referred to as SYN.J-13 water, was allowed to equilibrate with the atmosphere for at least 10 days. The synthetic groundwater had a pH of 8.4 and an alkalinity of  $25 \text{ meq L}^{-1}$ , and an ionic strength of 0.005 M.

## Colloidal Solutions

### *Iron Oxide and Montmorillonite Colloidal Solutions*

Commercial synthetic hematite ( $\text{Fe}_2\text{O}_3$ ) mineral powders (particle size  $< 1.0 \mu\text{m}$ ) were obtained from Nissan Chemical Industries Ltd. “Cheto” Ca-montmorillonite mineral powder (particle size of  $< 1.0 \mu\text{m}$ ) was obtained from University of Missouri, Columbia, Source Clay Repository, Clay Mineral Society. The synthetic hematite contains 99.62%  $\text{Fe}_2\text{O}_3$ ,  $< 0.05\%$   $\text{SiO}_2$ , and 0.44% water, as well as  $\text{CO}_2$  and volatile organic compounds. X-ray diffraction shows the mineral is a hematite. The montmorillonite mineral contained 52.0%  $\text{SiO}_2$ , 16.33%  $\text{Al}_2\text{O}_3$ , 1.34% Fe as  $\text{Fe}_2\text{O}_3$ , 5.16%  $\text{MgO}$ , 1.88%  $\text{CaO}$ , 0.98%  $\text{Na}_2\text{O}$ , 0.12%  $\text{K}_2\text{O}$ , 0.25%  $\text{TiO}_2$ , 14.38%  $\text{H}_2\text{O}$ , and 8.17% interlayer water, as well as  $\text{CO}_2$  and volatile organic compounds. X-ray diffraction showed that the mineral was a Ca-montmorillonite.

The colloidal solutions of hematite and montmorillonite were prepared by dispersing a certain amount of hematite or montmorillonite powder in a certain amount of nanopure deionized water in an ultrasonic bath for 3 minutes. The dispersed suspension was transferred to a one-liter cylinder and left undisturbed for 5 hours at room temperature to allow large particles to settle.



Thereafter, the supernatant solution was carefully collected as stock colloidal solution. The pH of both the hematite and “Cheto” montmorillonite colloidal solutions was 6.9. The mass of the colloid particles in the solutions was determined by the difference in the weights before and after vaporizing (air-drying) and oven-drying (105°C) of a given amount of each solution (Lu *et al.*, 1998a). Working colloidal solutions, referred to as Hematite.J-13, Hematite.SYN.J-13, Mont.J-13 and Mont.SYN.J-13, with a colloid concentration of 200 mg L<sup>-1</sup> were prepared by diluting a measured volume of stock colloidal solution into 1 liter of natural J-13 water or synthetic J-13. The particle size and surface charge (zeta potential) of hematite and montmorillonite colloids were measured using a Coulter LS-300 light-scattering system and a Coulter Delsa 440 SX mobility measuring system, respectively, at the University of New Mexico. The pH of each solution was measured again following dilution. The characterization of the colloidal solutions is given in Table 1. The total surface area was measured using the sorption procedure of ethylene glycol monoethyl ether (EGME) described by Carter (1996). The total surface area of the montmorillonite colloids was  $8.33 \times 10^5 \text{ m}^2 \text{ kg}^{-1}$ . The total surface area of the hematite colloids was  $5.35 \times 10^4 \text{ m}^2 \text{ kg}^{-1}$ .

### *Colloidal Silica Solutions*

Synthetic colloidal silica PST-1, was purchased from Nissan Chemical Industries Ltd. The solutions were manufactured by dispersing negatively charged amorphous silica particles in water. The particles were spherical, and the colloidal solution contained 40% SiO<sub>2</sub> and 60% water. The major surfactant of the colloidal silica was Na<sub>2</sub>O. To clean the colloidal silica of surfactants, the following dialysis procedure was used: approximately 50 ml of original colloidal

Table 1. Characterization of hematite, Ca- montmorillonite, and silica PST-1 colloidal solutions

	Hematite. J-13	Hematite. SYN.J-13	PST-1 J-13	PST-1 SYN.J-13	Mont. J-13	Mont. SYN.J-13
pH	8.19	8.31	8.20	8.30	8.22	8.31
Mass of Colloids (mg L <sup>-1</sup> )	200	200	200	200	200	200

Average Particle Size(nm)	70	70	100	100	100	100
Total Surface Area m <sup>2</sup> kg <sup>-1</sup>	5.35 x 10 <sup>4</sup>	5.35 x 10 <sup>4</sup>	1.14 x 10 <sup>6</sup>	1.14 x 10 <sup>6</sup>	8.33 x 10 <sup>5</sup>	8.33 x 10 <sup>5</sup>
Average Mobility (μm-cm/v-s)	-1.1±1.1	-2.8±0.8	-2.4±0.6	-2.5±2.1	-0.9±0.8	-2.3±0.8
Average Zeta Potential (mV)	-14.1±14.1	-35.3±12.8	-31.0±7.3	-32.5±27.9	-11.7±9.8	-29.1±9.9

solution was diluted to 200 ml with nanopure deionized water and transferred to a 12,000-14,000 molecular weight cut-off membrane, referred to as dialysis tubing. The tubing was sealed and placed in a container with nanopure deionized water. Measurements of the concentrations of Na, K, and Ca, and the conductivity of the solution before and after the dialysis process were used to verify the removal of the surfactants. The conductivity of the original colloidal solution was 9.27 mS. After the 50-day dialysis procedure, the conductivity of the cleaned colloidal solution was 4.9 μS. The pH of the cleaned silica colloidal solution was adjusted to 8.4 using a saturated Na<sub>2</sub>CO<sub>3</sub> solution. The mass of the colloids in the cleaned solution was determined by applying the same method used for the hematite and montmorillonite colloidal solutions. Two working colloidal solutions, referred to as PST-1.J-13 and PST-1.SYN.J-13 were prepared by diluting a specific volume of cleaned colloidal solution with natural groundwater or synthetic groundwater. The particle size and zeta potential of colloidal particles were determined in the same way as the hematite and montmorillonite. The characterizations of the colloidal solutions are given in Table 1. The total surface area was measured using an ethylene glycol monoethyl ether (EGME) sorption procedure described by Carter (1996). The total surface area of the PST-1 silica was 1.14 x 10<sup>6</sup> m<sup>2</sup> kg<sup>-1</sup>. The pH values of the two silica colloidal solutions were 8.2 for PST-1.J-13 and 8.3 for PST-1 SYN.J-13. Stabilization of the colloids was achieved by the repulsion between the negative surface charges of the colloids (Nissan Chemical Ind., 1994). Aggregation of silica colloids in the manufactured colloidal solution occurred after 6 months.

### Tracer Solutions

The Pu(V) stock solution contained  $7.65 \times 10^{-4}$  M of Pu and was comprised of 99.7% Pu(V), and 0.3% Pu(VI), and contained 93.9%  $^{239}\text{Pu}$ . Two diluted Pu(V) working solutions, referred to as Pu(V).J-13 and Pu(V).SYN.J-13, were prepared. The concentration of Pu in the two solutions was  $2.74 \times 10^{-7}$  M. The activities of the work solutions were determined using a Packard Tri-Cab liquid scintillation counter (LSC). The alpha activity of Pu(V) was 3461.4 pCi/g in Pu(V).J-13 and 3372.7 pCi/g in Pu(V).SYN.J-13. The pH values of the two solutions were 8.22.

The concentration of  $^{243}\text{Am}$  stock was  $4.94 \times 10^{-6}$  M Am of which 100% was Am(III). Two diluted Am(III) working solutions, referred to as Am.J-13 and Am.SYN.J-13, were prepared. The concentration of Am was  $9.86 \times 10^{-9}$  M in the Am.J-13 solution and  $4.94 \times 10^{-9}$  M in the Am.SYN.J-13 solution. The activities of these two solutions were analyzed using the LSC. The alpha activity of Am was 442.8 pCi/g in the Am.J-13 and 428.03 pCi/g in the Am.SYN.J-13. The pH values of these two solutions were 8.22 and 8.47, respectively.

The Np(V) stock solution contained 0.025 M of  $^{237}\text{Np}$  of which 99.7% was Np(V). Two diluted Np(V) working solutions, referred to as Np(V).J-13 and Np(V).SYN.J-13, were prepared. The concentration of  $^{237}\text{Np}$  in the two solutions was  $1.9 \times 10^{-7}$  M. The activities of the work solutions were determined using the LSC. The alpha activity of Np(V) was 3072.6 pCi/g in Np(V).J-13 and 3034.3 pCi/g in Np(V).SYN.J-13. The pH values of the two solutions were 8.07 and 8.15, respectively.

The  $^{238}\text{U}$  stock was  $4.2 \times 10^{-3}$  M in  $\text{HNO}_3$  with 99.27%  $^{238}\text{U(VI)}$ , 0.72%  $^{235}\text{U}$  and 0.0055%  $^{234}\text{U}$ . One diluted solution ( $4.2 \times 10^{-4}$  M), referred to as U(VI).DI, was prepared by diluting 10 ml of stock solution into 100-ml nanopure deionized water. Two additional diluted working solutions, referred as U(VI).J-13 and U(VI).SYN.J-13, were prepared using U(VI).DI solution. The concentration of U in the solutions was analyzed using a kinetic phosphorescence analyzer (KPA-11). The total concentration of U was  $1.425 \times 10^{-5}$  M in the U.J-13 and  $1.457 \times 10^{-5}$  M in the U.SYN.J-13. The pH values of these two solutions were 8.039 and 8.165,

respectively. Throughout the experiments, the activities of the  $^{239}\text{Pu}$ ,  $^{237}\text{Np}$ ,  $^{243}\text{Am}$ , or  $^{238}\text{U}$  working solutions were frequently measured.

## Sorption Procedures

### *Kinetics Experiments*

Kinetics experiments were performed in duplicate to examine the adsorption kinetics of  $^{239}\text{Pu(V)}$ ,  $^{243}\text{Am(III)}$ ,  $^{237}\text{Np(V)}$  and  $^{238}\text{U(VI)}$  onto hematite, montmorillonite and silica colloids. The colloid concentrations were always adjusted to  $200\text{ mg L}^{-1}$ . 20-mL aliquots of hematite, montmorillonite, and silica colloidal solutions, in both J-13 and SYN.J-13 waters, were combined with 1 mL aliquots of  $^{239}\text{Pu(V)}$ ,  $^{243}\text{Am(III)}$ ,  $^{237}\text{Np(V)}$ , and  $^{238}\text{U(VI)}$  working solutions, and were placed into Oak Ridge centrifuge tubes (50-mL) and agitated on an orbital shaker at 150 rpm. The contact periods for the colloids and radionuclides were 1, 4, 24, 48, 96, and 240 hours. At the same time, control samples were also prepared using 20-mL portions of colloid-free J-13, or SYN.J-13 water and 1 mL portion of  $^{239}\text{Pu}$ - $^{243}\text{Am}$ -,  $^{237}\text{Np}$ - and  $^{238}\text{U}$ -working solutions. At the end of each contact period, the samples and controls were centrifuged. The amount of time and force needed to separate colloid particles from a well-dispersed suspension is calculated using Stock's law. To separate colloids with diameters  $\geq 28\text{ nm}$ , suspended in Oak Ridge tubes of the length used, Stock's Law dictates the samples would require two iterations of centrifugation at 38,300 g for 2 hours each iteration. At the end of the second centrifugation, approximately 10 ml of the supernatant was collected for measurements of  $^{239}\text{Pu}$ ,  $^{243}\text{Am}$ ,  $^{237}\text{Np}$ , and  $^{238}\text{U}$  activity, or concentration, remaining in the solution phase and for pH. The  $\alpha$  activity of  $^{239}\text{Pu(V)}$ ,  $^{243}\text{Am(III)}$ , and  $^{237}\text{Np(V)}$  was analyzed using the LSC. The concentration of  $^{238}\text{U(VI)}$  in solution was analyzed using a KPA-11. The adsorbed values of  $^{239}\text{Pu}$ ,  $^{243}\text{Am}$ ,  $^{237}\text{Np}$ , and  $^{238}\text{U}$  onto hematite, montmorillonite, and silica colloids were corrected for the adsorption to the tube walls using results from control samples.

The sorption distribution coefficient ( $K_d$ -value) of  $^{239}\text{Pu}$ ,  $^{243}\text{Am}$ ,  $^{237}\text{Np}$ , and  $^{238}\text{U}$  on hematite, montmorillonite, and silica colloids is calculated using the following equation (Lu, *et al.*, 1998a):

$$K_d\text{-value (ml g}^{-1}\text{)} = [(A_0V_0 - A_fV_f)/M]/A_f \quad [5]$$

where  $A_0$  is the initial  $\alpha$  activity (or concentration) of  $^{239}\text{Pu}$ ,  $^{243}\text{Am}$ ,  $^{237}\text{Np}$ , and  $^{238}\text{U}$  per milliliter of solution;  $V_0$  is the initial volume (ml) of the solution in contact with the colloid particles;  $A_f$  is the final  $\alpha$  activity (or concentration) of  $^{239}\text{Pu}$ ,  $^{243}\text{Am}$ ,  $^{237}\text{Np}$ , and  $^{238}\text{U}$  per ml solution after sorption (minus the activity or concentration of  $^{239}\text{Pu}$ ,  $^{243}\text{Am}$ ,  $^{237}\text{Np}$ , and  $^{238}\text{U}$ , which sorbed to the Oak Ridge tube walls; determined from the controls);  $V_f$  is the final volume (ml) of the solution after sorption; and  $M$  (g) is the mass of colloids used in the sorption process.

### *Temperature Experiments*

The temperature experiments were performed at  $20^\circ\text{C}$ ,  $40^\circ\text{C}$ , and  $80^\circ\text{C}$  to examine the influence of temperature on the adsorption of  $^{239}\text{Pu(V)}$ ,  $^{243}\text{Am(III)}$ ,  $^{237}\text{Np(V)}$ , and  $^{238}\text{U(VI)}$  onto colloids of hematite, montmorillonite and silica in natural groundwater. The experiments were conducted in duplicate. 20-mL aliquots of hematite, montmorillonite, and silica colloidal solutions, in J-13 water, were combined with 1 mL aliquots of  $^{239}\text{Pu(V)}$ -,  $^{243}\text{Am(III)}$ -,  $^{237}\text{Np(V)}$ -, and  $^{238}\text{U(VI)}$ -J-13 working solutions, and were placed into Oak Ridge centrifuge tubes (50-mL). The tubes were then placed in a temperature-control block and agitated on an orbital shaker at 150 rpm for 240 hours. At the same time, control samples were prepared using 20-mL portions of colloid-free J-13 water combined with 1 mL portions of the actinide working solutions. After 240 hours, the colloids were separated from liquid phase by applying the same centrifugation method used in the kinetics experiments. The same method was applied to measure the  $\alpha$  activity, or concentration, of these four actinides. The pH values of the solutions

were also measured. The adsorbed values of  $^{239}\text{Pu}$ ,  $^{243}\text{Am}$ ,  $^{237}\text{Np}$ , and  $^{238}\text{U}$  onto colloids of hematite, montmorillonite, and silica were corrected with results from control samples.

### *Ionic Strength Experiments*

The ionic strength experiments were performed at room temperature to examine the influence of the ionic strength of the water on the adsorption of  $^{239}\text{Pu(V)}$ ,  $^{243}\text{Am(III)}$ ,  $^{237}\text{Np(V)}$ , and  $^{238}\text{U(VI)}$  onto hematite, montmorillonite, and silica colloids in natural groundwater. Based on the chemical composition of J-13 water, four synthetic J-13 waters with different ionic strengths were prepared by dissolving the same amounts of  $\text{NaHCO}_3$ ,  $\text{MgSO}_4$ ,  $\text{KNO}_3$ ,  $\text{SiO}_2$ , but varying the amount of  $\text{CaCl}_2$ , in nanopure deionized water. The ionic strengths of the resulting synthetic solutions were  $4.71 \times 10^{-3}$ ,  $1.7 \times 10^{-2}$ ,  $7.11 \times 10^{-2}$ , and  $1.34 \times 10^{-1}$  M. We did not use  $\text{NaCl}$  to adjust the ionic strength because  $\text{NaCl}$  might have caused the interlayers of the montmorillonite to swell. The  $^{239}\text{Pu(V)}$ -,  $^{243}\text{Am(III)}$ -,  $^{237}\text{Np(V)}$ -, and  $^{238}\text{U(VI)}$ -DI working solutions were prepared by diluting the stock solutions of  $^{239}\text{Pu(V)}$ ,  $^{243}\text{Am(III)}$ ,  $^{237}\text{Np(V)}$ , and  $^{238}\text{U(VI)}$  in nanopure deionized water. The resulting  $^{239}\text{Pu(V)}$ ,  $^{243}\text{Am(III)}$ ,  $^{237}\text{Np(V)}$ , and  $^{238}\text{U(VI)}$  concentrations were  $2.74 \times 10^{-7}$  M for  $^{239}\text{Pu(V)}$ .DI,  $9.85 \times 10^{-9}$  M for  $^{243}\text{Am(III)}$ .DI,  $1 \times 10^{-7}$  M for  $^{237}\text{Np(V)}$ .DI, and  $1.42 \times 10^{-5}$  M for  $^{238}\text{U(VI)}$ .DI

The experiments were conducted in duplicate. 20-mL aliquots of hematite, montmorillonite, and silica colloidal solutions in SYN.J-13 waters with different ionic strengths, were combined with 1 mL aliquots of  $^{239}\text{Pu(V)}$ -,  $^{243}\text{Am(III)}$ -,  $^{237}\text{Np(V)}$ -, and  $^{238}\text{U(VI)}$ -DI working solutions and were placed into Oak Ridge centrifuge tubes (50-mL) and agitated on an orbital shaker at 150 rpm for 240 hours. At the same time, control samples were prepared using 20-mL portions of colloids-free SYN.J-13 waters combined with 1 mL portions of the actinide working solutions. After 240 hours, the colloids were separated by applying the same centrifugation method used in the kinetics experiments. The  $\alpha$  activity, or concentration, of  $^{239}\text{Pu(V)}$ ,  $^{243}\text{Am(III)}$ ,  $^{237}\text{Np(V)}$ , and  $^{238}\text{U(VI)}$  was analyzed by LSC or KPA and the pH values of the solutions were also measured. The adsorbed values of  $^{239}\text{Pu}$ ,  $^{243}\text{Am}$ ,  $^{237}\text{Np}$ , and  $^{238}\text{U}$

onto colloids of hematite, montmorillonite, and silica were corrected with results from the control samples.

### *Colloid Concentration Experiments*

The colloid concentration experiments were performed at room temperature to examine the influence of colloid concentration on the adsorption of  $^{239}\text{Pu(V)}$  and  $^{243}\text{Am(III)}$  onto colloids of hematite, montmorillonite, and silica in natural and synthetic groundwater (the ionic strength was 0.005 M). The colloid concentrations were 10, 50, 100, 150, 200, and 1000  $\text{mg L}^{-1}$ . The experiments were conducted in duplicate. 20-mL aliquots of hematite, montmorillonite, and silica colloidal solutions, in both J-13 and SYN.J-13 waters and with different colloid concentrations, were combined with 1 mL aliquots of  $^{239}\text{Pu(V)}$ - and  $^{243}\text{Am(III)}$ -J-13 or SYN.J-13 working solutions and were placed into Oak Ridge centrifuge tubes (50-mL) where they were agitated on an orbital shaker at 150 rpm for 240 hours. At the same time, control samples were prepared using 20-mL portions of colloids-free J-13 and SYN.J-13 waters combined with 1 mL portions of  $^{239}\text{Pu(V)}$ - and  $^{243}\text{Am(III)}$ -J-13 and SYN.J-13 working solutions. After 240 hours, the colloids were separated by applying the same centrifugation method used in the kinetics experiments. The  $\alpha$  activity of  $^{239}\text{Pu(V)}$  and  $^{243}\text{Am(III)}$  was analyzed using LSC. The pH of the solutions was also measured. The adsorbed values of  $^{239}\text{Pu}$  and  $^{243}\text{Am}$  onto colloids of hematite, montmorillonite, and silica were corrected with results from control samples.

### **Desorption Procedure**

Desorption experiments were conducted in duplicate under the same conditions as the kinetics experiments. The  $^{239}\text{Pu}$ -,  $^{243}\text{Am}$ -,  $^{237}\text{Np}$ -, and  $^{238}\text{U}$ -loaded colloid particles were collected from the 240 hours sorption in the kinetics experiments. At the end of the sorption process, the colloid particles were separated from the liquid phase by centrifuging at 38,300 g for 2 hours. Most of the supernatant was carefully removed, and the wet weights of the colloids were obtained. The colloid samples were then extracted with 10 ml aliquots of the radionuclide-free J-13 and SYN.J-13 water. Desorption of  $^{239}\text{Pu}$ ,  $^{243}\text{Am}$ ,  $^{237}\text{Np}$ , and  $^{238}\text{U}$  was allowed to

proceed 293 days for  $^{239}\text{Pu}$ , 200 days for  $^{243}\text{Am}$ , 212 days for  $^{237}\text{Np}$  and 212 days for  $^{238}\text{U}$ . At the end of desorption process, the extracts were separated by applying the same centrifugation procedure used in the sorption experiments. The  $\alpha$  activity of  $^{239}\text{Pu}$ ,  $^{243}\text{Am}$ , and  $^{237}\text{Np}$  in the extracts was measured using LSC. The concentration of  $^{238}\text{U}$  in the solution was measured using the KPA.

## RESULTS

### Actinide Adsorption Kinetics

#### *Adsorption Kinetics of $^{239}\text{Pu}$*

Adsorption of  $^{239}\text{Pu}$  onto hematite in natural groundwater was slower and occurred at a lower level than in synthetic groundwater. The hematite colloids sorbed 46% of the  $^{239}\text{Pu}$  in natural groundwater during the first hour (Fig. 1). At the end of the sorption process (240 hrs), 95% of the  $^{239}\text{Pu}$  was adsorbed by hematite colloids. The adsorption distribution coefficient ( $K_d$ -value) reached  $(1.1 \pm 0.03) \times 10^5 \text{ ml g}^{-1}$  in natural groundwater (Table 2).

The hematite colloids sorbed 96% of the  $^{239}\text{Pu}$  in the synthetic groundwater during the first hour (Fig. 1). After 1 hour, the amount of the adsorbed  $^{239}\text{Pu}$  increased gradually with time



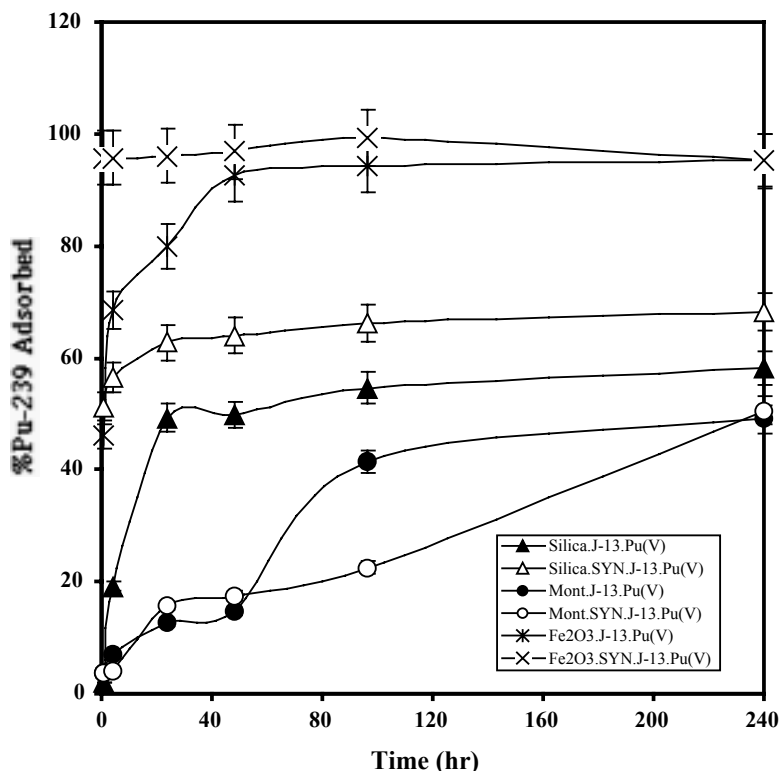


Fig. 1. Percentage of  $^{239}\text{Pu}$  adsorbed onto colloids of hematite, montmorillonite, and silica as a function of time in natural and synthetic groundwater (colloidal concentration:  $200 \text{ mg L}^{-1}$ )

and reached a maximum of  $\sim 99.2\%$  at 96 hours, then it decreased slightly to 95% during the remaining 144 hours. At first, this behavior seems to indicate that partial desorption of  $^{239}\text{Pu}$  from hematite colloids occurred after 96 hours. At the time of maximum sorption (96 hrs), the sorption distribution coefficient of  $^{239}\text{Pu}$  ( $K_d$ -value) was  $(7.0 \pm 0.03) \times 10^5$  (Table 2).

Adsorption of  $^{239}\text{Pu}$  onto montmorillonite colloids was slower than onto hematite and silica colloids in both natural and synthetic groundwater. The montmorillonite colloids sorbed only  $\sim 3.7\%$  of the  $^{239}\text{Pu}$  in both natural and synthetic groundwater during the first hour (Fig. 1).

After 1 hour, the amount of the adsorbed  $^{239}\text{Pu}$  increased gradually with time. At the end of the sorption process (240 hrs),  $\sim 50\%$  of the  $^{239}\text{Pu}$  was adsorbed by montmorillonite colloids in both waters. The adsorption distribution coefficient ( $K_d$ -value) reached  $(5.8 \pm 1.11) \times 10^3 \text{ ml g}^{-1}$  in natural groundwater and  $(6.5 \pm 2.37) \times 10^3 \text{ ml g}^{-1}$  in synthetic groundwater. The  $K_d$ -values of

the  $^{239}\text{Pu}$  on the montmorillonite colloids were  $\sim 10^2$  orders lower than that on the hematite colloids (Table 2).

Table 2. Adsorption distribution coefficients ( $K_d$ -values,  $\text{ml g}^{-1}$ ) of  $^{239}\text{Pu}$  on colloids of hematite, montmorillonite, and silica as a function of time in natural and synthetic groundwater

Time (hr)	Hematite J-13	Hematite SYN.J-13	Mont. J-13	Mont. SYN.J-13	Silica. J-13	Silica. SYN.J-13
1	$(4.9 \pm 0.05) \times 10^3$	$(1.3 \pm 0.03) \times 10^5$	$(2.3 \pm 0.2) \times 10^2$	$(2.3 \pm 0.3) \times 10^2$	$(1.2 \pm 0.04) \times 10^2$	$(6.1 \pm 0.2) \times 10^3$
4	$(1.3 \pm 0.07) \times 10^4$	$(1.3 \pm 0.05) \times 10^5$	$(4.4 \pm 1.5) \times 10^2$	$(2.4 \pm 0.6) \times 10^2$	$(1.7 \pm 1.1) \times 10^3$	$(2.6 \pm 0.3) \times 10^3$
24	$(2.3 \pm 0.2) \times 10^4$	$(1.5 \pm 0.2) \times 10^5$	$(8.2 \pm 0.8) \times 10^2$	$(1.1 \pm 0.3) \times 10^3$	$(5.5 \pm 0.1) \times 10^3$	$(9.9 \pm 0.5) \times 10^3$
48	$(7.5 \pm 0.7) \times 10^4$	$(1.7 \pm 0.0) \times 10^5$	$(1.0 \pm 0.03) \times 10^3$	$(1.2 \pm 0.01) \times 10^3$	$(5.8 \pm 0.2) \times 10^3$	$(9.9 \pm 0.5) \times 10^3$
96	$(9.7 \pm 1.7) \times 10^4$	$(7.0 \pm 0.03) \times 10^5$	$(4.0 \pm 0.7) \times 10^3$	$(1.7 \pm 0.1) \times 10^3$	$(6.7 \pm 0.03) \times 10^3$	$(1.2 \pm 0.004) \times 10^4$
240	$(1.1 \pm 0.03) \times 10^5$	$(1.2 \pm 0.3) \times 10^5$	$(5.8 \pm 1.1) \times 10^3$	$(6.5 \pm 2.4) \times 10^3$	$(8.1 \pm 0.01) \times 10^3$	$(1.5 \pm 0.6) \times 10^4$

Note: Original data in Table 2 from file "Sorption#1;99-00,Pu(V)/Coll., Sorption#1-1;99-00,Time.". The calculation of statistic errors in the Table, referred as to Standard Deviation of Mean, is shown in the file "Pu/Am.Time.Kd.Std.Dv.Mean. 99-00".

Adsorption of  $^{239}\text{Pu}$  onto silica colloids was slower than onto hematite colloids, but faster than onto montmorillonite colloids in both natural and synthetic groundwater (Fig. 1). The silica colloids sorbed only  $\sim 2\%$  of the  $^{239}\text{Pu}$  in natural groundwater during the first hour (Fig. 1). After 1 hour, the amount of the adsorbed  $^{239}\text{Pu}$  increased gradually with time. At the end of the sorption process (240 hrs),  $\sim 58\%$  of the  $^{239}\text{Pu}$  was adsorbed by silica colloids in natural groundwater. The  $K_d$ -value of the  $^{239}\text{Pu}$  on the silica colloids was  $(8.1 \pm 1.11) \times 10^3 \text{ ml g}^{-1}$ , which was 13.6 times lower than that on the hematite colloids in natural groundwater (Table 2). In synthetic groundwater, the silica colloids sorbed  $\sim 51\%$  of the  $^{239}\text{Pu}$  during the first hour (Fig. 1). After 1 hour, the amount of the adsorbed  $^{239}\text{Pu}$  increased gradually with time. At the end of

the sorption process (240 hrs), ~68% of the  $^{239}\text{Pu}$  was adsorbed. The  $K_d$ -value of  $^{239}\text{Pu}$  on the silica colloids was  $(1.5 \pm 0.6) \times 10^4$ , which was about 10 times lower than that on the hematite colloids in synthetic groundwater (Table 2).

### Adsorption Kinetics of $^{243}\text{Am}$

Adsorption of  $^{243}\text{Am}$  onto hematite colloids was a fast process in both natural and synthetic groundwater. The hematite colloids sorbed ~100% of the  $^{243}\text{Am}$  in both groundwaters during the first hour (Fig. 2). After 1 hour, the amount of the adsorbed  $^{243}\text{Am}$  decreased gradually with time. At the end of the sorption process, ~90% of the  $^{243}\text{Am}$  was adsorbed in natural groundwater and 93% of the  $^{243}\text{Am}$  was adsorbed in synthetic groundwater. At the time of maximum sorption (first hour), the  $K_d$ -value of the  $^{243}\text{Am}$  reached  $(1.0 \pm 0.0) \times 10^7 \text{ ml g}^{-1}$  in natural groundwater and  $(5.4 \pm 0.8) \times 10^6 \text{ ml g}^{-1}$  in synthetic groundwaters (Table 3).

Montmorillonite colloids sorbed less  $^{243}\text{Am}$  than hematite colloids did in both natural and synthetic groundwater. During the first hour, montmorillonite colloids sorbed ~61% of the  $^{243}\text{Am}$  in natural groundwater and ~79% in synthetic groundwater (Fig. 2). After 1 hour, the

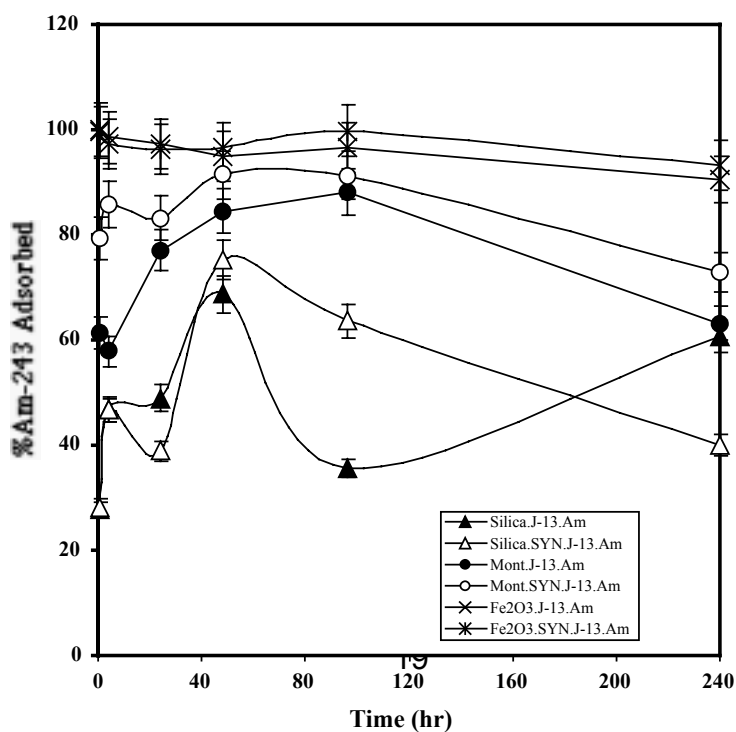


Fig.2. Percentage of  $^{243}\text{Am}$  adsorbed onto colloids of hematite, montmorillonite, and silica as a function of time in natural and synthetic groundwater (colloidal concentration:  $200 \text{ mg L}^{-1}$ )

Table 3. Adsorption distribution coefficients ( $K_d$ -values,  $\text{ml g}^{-1}$ ) of  $^{243}\text{Am}$  on colloids of hematite, montmorillonite, and silica as a function of time in natural and synthetic groundwater

Time (hr)	Hematite J-13	Hematite SYN.J-13	Mont. J-13	Mont. SYN.J-13	Silica. J-13	Silica. SYN.J-13
1	$(1.0 \pm 0.0) \times 10^7$	$(5.4 \pm 3.6) \times 10^6$	$(2.7 \pm 0.8) \times 10^3$	$(2.5 \pm 0.5) \times 10^4$	$(1.8 \pm 0.4) \times 10^3$	$(2.4 \pm 0.2) \times 10^3$
4	$(3.9 \pm 0.8) \times 10^5$	$(2.7 \pm 0.6) \times 10^5$	$(7.1 \pm 0.08) \times 10^3$	$(4.2 \pm 0.2) \times 10^4$	$(4.5 \pm 0.04) \times 10^3$	$(6.0 \pm 0.07) \times 10^3$
24	$(2.7 \pm 0.6) \times 10^5$	$(2.0 \pm 0.2) \times 10^5$	$(2.4 \pm 0.3) \times 10^4$	$(4.6 \pm 1.5) \times 10^4$	$(7.4 \pm 2.3) \times 10^3$	$(5.0 \pm 0.3) \times 10^3$
48	$(2.0 \pm 0.5) \times 10^5$	$(5.1 \pm 2.7) \times 10^5$	$(6.5 \pm 2.4) \times 10^4$	$(1.1 \pm 0.2) \times 10^5$	$(2.1 \pm 0.2) \times 10^4$	$(3.2 \pm 0.8) \times 10^4$
96	$(3.2 \pm 1.3) \times 10^5$	$(6.2 \pm 2.9) \times 10^6$	$(1.0 \pm 0.5) \times 10^5$	$(1.0 \pm 0.05) \times 10^5$	$(4.6 \pm 0.1) \times 10^3$	$(2.0 \pm 0.6) \times 10^4$
240	$(7.9 \pm 1.3) \times 10^4$	$(1.2 \pm 0.1) \times 10^5$	$(1.4 \pm 0.004) \times 10^4$	$(2.3 \pm 0.06) \times 10^4$	$(1.2 \pm 0.05) \times 10^4$	$(5.6 \pm 0.9) \times 10^3$

Note: Original data in Table 3 from file "Sorption#2;99-00, Am/Coll., Sorption#2-1;99-00,Time." The calculation of statistic errors in the Table, referred as to Standard Deviation of Mean, is shown in the file "Pu/Am. Time.Kd.Std. Dv.Mean. 99-00".

amount of the adsorbed  $^{243}\text{Am}$  increased gradually with time and reached a maximum of ~88.2% in natural groundwater and ~99.2% in synthetic groundwater at 96 hours, then it decreased to ~73% in natural groundwater and ~93% in synthetic groundwater during the remaining 144 hours. This indicates that partial desorption of  $^{243}\text{Am}$  from montmorillonite colloids occurred after 96 hours. At the time of maximum sorption (96 hrs), the  $K_d$ -value of the  $^{243}\text{Am}$  was  $(1.4 \pm 0.004) \times 10^3 \text{ ml g}^{-1}$  in natural groundwater and was  $(2.3 \pm 0.06) \times 10^4 \text{ ml g}^{-1}$  in synthetic groundwater (Table 3).

The silica colloids sorbed less  $^{243}\text{Am}$  than the hematite and the montmorillonite colloids in both natural and synthetic groundwater. During the first hour, silica colloids sorbed ~28%

of the  $^{243}\text{Am}$  in both natural and synthetic groundwater (Fig. 2). After 1 hour, the amount of the adsorbed  $^{243}\text{Am}$  increased gradually with time and reached a maximum of ~69% in natural groundwater and ~75% in synthetic groundwater at 48 hours. After that, adsorption of  $^{243}\text{Am}$  decreased with time and dropped to 40% at the end of the sorption process (240 hrs) in synthetic groundwater. This indicates that partial desorption of  $^{243}\text{Am}$  from silica colloids occurred after 48 hours in synthetic groundwater. At the time of maximum sorption (48hrs), the  $K_d$ -value of  $^{243}\text{Am}$  on silica colloids was  $(3.2 \pm 0.8) \times 10^4 \text{ ml g}^{-1}$  in synthetic groundwater (Table 3). However, in natural groundwater, adsorption of  $^{243}\text{Am}$  showed fluctuation. The amount of the adsorbed  $^{243}\text{Am}$  dropped to ~36% at 96 hours, then it increased to ~61% at the end of the sorption process (240 hours). At the time of the maximum sorption (48hrs), the  $K_d$ -value of the  $^{243}\text{Am}$  on silica colloids was  $(2.1 \pm 0.2) \times 10^4 \text{ ml g}^{-1}$ , which was 10 times lower than  $K_d$ -values on hematite colloids (Table 3).

#### *Adsorption Kinetics of $^{237}\text{Np}$*

Generally, adsorption of  $^{237}\text{Np}$  by all three types of colloids was slower and occurred at lower levels than adsorption of  $^{239}\text{Pu}$  and  $^{243}\text{Am}$  in both natural and synthetic groundwater. Adsorption of  $^{237}\text{Np}$  by hematite colloids occurred at higher levels and was faster than by montmorillonite and silica colloids. Moreover, hematite sorbed much more  $^{237}\text{Np}$  in synthetic groundwater (12% more) than in natural groundwater. In synthetic groundwater, hematite colloids sorbed ~20.4% of the  $^{237}\text{Np}$  during the first hour (Fig. 3). Thereafter, the amount of the adsorbed  $^{237}\text{Np}$  increased and reached a maximum of ~29% at 48 hours, and then it dropped to ~26% at 96 hours, then back up to ~28% at 240 hours. At the time of the maximum adsorption (48 hrs), the  $K_d$ -value was  $(2.2 \pm 0.07) \times 10^3 \text{ ml g}^{-1}$  (Table 4). In natural groundwater, adsorption of  $^{237}\text{Np}$  by hematite colloids showed more fluctuation. During the first hour, hematite colloids sorbed ~8.3% of the  $^{237}\text{Np}$ , and then the amount of the adsorbed  $^{237}\text{Np}$

dropped to ~6.5% at 4 hours (Fig. 3). Thereafter, the amount of the adsorbed  $^{237}\text{Np}$  increased up to 12.5% at 48 hours, and then it dropped again to ~8.9% at 96 hours. At the end of the sorption process, hematite sorbed ~13.5% of the  $^{237}\text{Np}$  in natural groundwater, and the  $K_d$ -value reached  $(8.8 \pm 2.4) \times 10^2 \text{ ml g}^{-1}$  (Table 4).

Very little  $^{237}\text{Np}$  was adsorbed by montmorillonite colloids in both natural and synthetic groundwater. Montmorillonite colloids sorbed ~1.7% of the  $^{237}\text{Np}$  in both natural and synthetic groundwater during the first hour (Fig. 3). The amount of the adsorbed  $^{237}\text{Np}$  did not change much during the next 23 hours, but reached a maximum of ~4% at 48 hours in natural

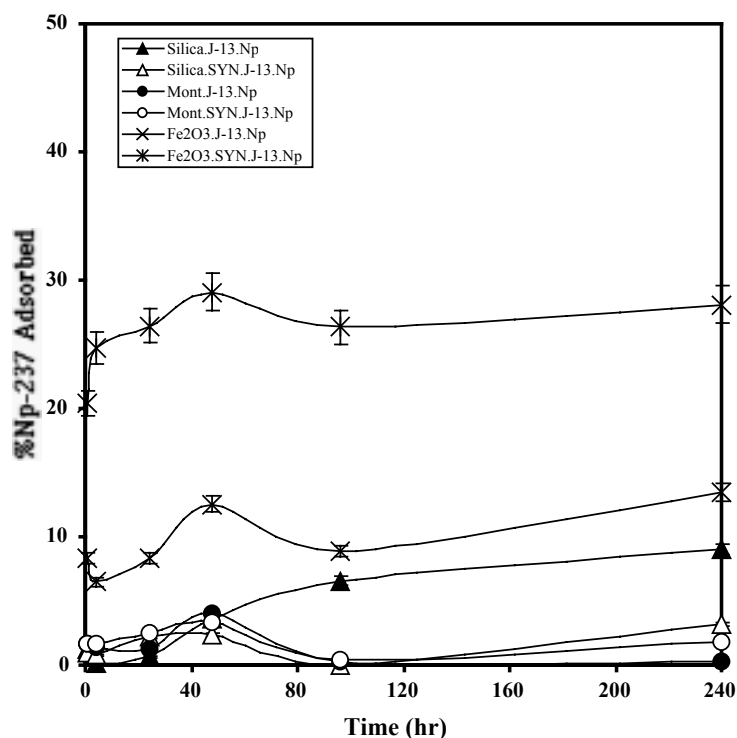


Fig. 3. Percentage of  $^{237}\text{Np}$  adsorbed onto colloids of hematite, montmorillonite, and silica as a function of time in natural and synthetic groundwater (colloidal concentration:  $200 \text{ mg L}^{-1}$ )

groundwater. Then the amount of the adsorbed  $^{237}\text{Np}$  dropped to 0.3% at 240 hours. At the time of maximum adsorption (48hrs), the  $K_d$ -value was  $(2.2 \pm 0.08) \times 10^2 \text{ ml g}^{-1}$  (Table 4). In synthetic groundwater, the amount of the adsorbed  $^{237}\text{Np}$  increased slightly after the first hour

and reached a maximum of 3.3% at 48 hours. Thereafter, the amount of the adsorbed  $^{237}\text{Np}$  dropped to 0.4% at 96 hours, and then it increased up to 1.9% at the end of sorption process. At the time of maximum adsorption (48hrs), the  $K_d$ -value was  $(1.8 \pm 0.5) \times 10^2 \text{ ml g}^{-1}$  (Table 4). Adsorption of  $^{237}\text{Np}$  by silica colloids was slow and occurred at low levels in both natural and synthetic groundwater, although it tended to increase with time. At the end of the sorption process (240 hrs), ~9% of the  $^{237}\text{Np}$  was adsorbed in natural groundwater, and ~3% of the  $^{237}\text{Np}$  was adsorbed in synthetic groundwater (Fig. 3). The  $K_d$ -values of  $^{237}\text{Np}$  on the silica colloids at the time of maximum adsorption (240 hrs) was  $(5.5 \pm 0.7) \times 10^2 \text{ ml g}^{-1}$  in natural groundwater and  $(1.9 \pm 0.1) \times 10^2 \text{ ml g}^{-1}$  in synthetic groundwater (Table 4).

Table 4. Adsorption distribution coefficients ( $K_d$ -values,  $\text{ml g}^{-1}$ ) of  $^{237}\text{Np}$  on colloids of hematite, montmorillonite, and silica as a function of time in natural and synthetic groundwater

Time (hr)	Hematite J-13	Hematite SYN.J-13	Mont. J-13	Mont. SYN.J-13	Silica. J-13	Silica SYN.J-13
1	$(4.8 \pm 0.2) \times 10^2$	$(1.4 \pm 0.04) \times 10^3$	$(9.4 \pm 5.4) \times 10^1$	$(9.0 \pm 2.6) \times 10^1$	$(7.2 \pm 4.3) \times 10^1$	$(5.4 \pm 1.9) \times 10^1$
4	$(3.8 \pm 0.6) \times 10^2$	$(1.8 \pm 0.01) \times 10^3$	$(7.5 \pm 0.7) \times 10^1$	$(8.9 \pm 0.03) \times 10^1$	$(9.8 \pm 0.2) \times 10^0$	$(4.2 \pm 1.4) \times 10^1$
24	$(5.0 \pm 0.4) \times 10^2$	$(1.9 \pm 0.06) \times 10^3$	$(7.4 \pm 1.9) \times 10^1$	$(1.4 \pm 0.2) \times 10^2$	$(3.6 \pm 0.1) \times 10^1$	$(1.2 \pm 0.3) \times 10^2$
48	$(7.6 \pm 0.05) \times 10^2$	$(2.2 \pm 0.02) \times 10^3$	$(2.2 \pm 0.08) \times 10^2$	$(1.8 \pm 0.5) \times 10^2$	$(2.0 \pm 0.5) \times 10^2$	$(1.3 \pm 0.2) \times 10^2$
96	$(5.4 \pm 0.5) \times 10^2$	$(2.0 \pm 0.02) \times 10^3$	$(1.5 \pm 0.9) \times 10^1$	$(2.1 \pm 0.9) \times 10^1$	$(3.9 \pm 1.4) \times 10^2$	$(3.0 \pm 1.4) \times 10^0$
240	$(8.8 \pm 2.4) \times 10^2$	$(2.2 \pm 0.07) \times 10^3$	$(1.4 \pm 0.2) \times 10^1$	$(1.1 \pm 0.6) \times 10^1$	$(5.5 \pm 0.7) \times 10^2$	$(1.9 \pm 0.1) \times 10^2$

Note: Original data in Table 4 from file "Sorption#3;99-00,Np(V)/Coll., Sorption#3-1;99-00,Time.". The calculation of statistic errors in the Table, referred as to Standard Deviation of Mean, is shown in the file "Np/U.Time. $K_d$ .Std. Dv. Mean. 99-00".

### Adsorption Kinetics of $^{238}\text{U}$

Generally, adsorption of  $^{238}\text{U}$  by all three types of colloids was much slower and occurred at lower levels than adsorption of  $^{239}\text{Pu}$  and  $^{243}\text{Am}$  in both natural and synthetic groundwater. Silica colloids sorbed more  $^{238}\text{U}$  than hematite and montmorillonite colloids did. Adsorption of  $^{238}\text{U}$  by hematite colloids showed fluctuation in both natural and synthetic groundwater. In natural groundwater, hematite colloids sorbed  $\sim 5\%$  of the  $^{238}\text{U}$  during the first hour, then the amount of the adsorbed  $^{238}\text{U}$  increased to  $\sim 7\%$  at 4 hours (Fig. 4). After that, it decreased during the period between 4 to 48 hours, and then increased and reached a maximum adsorption of  $\sim 7.6\%$  at 96 hours. The amount of the adsorbed  $^{238}\text{U}$  dropped to  $\sim 5\%$  at the end of sorption process. At the time of maximum adsorption (96 hrs), the  $K_d$ -value was  $(4.4 \pm 0.008) \times 10^2 \text{ ml g}^{-1}$  (Table 5). In synthetic groundwater, hematite colloids sorbed  $\sim 8\%$  of the  $^{238}\text{U}$  during the first hour (Fig. 3). Thereafter, the amount of adsorbed  $^{238}\text{U}$  tended to decrease with time. At the time of maximum sorption (1hr), the  $K_d$ -value was  $(4.9 \pm 0.7) \times 10^2 \text{ ml g}^{-1}$  (Table 5).

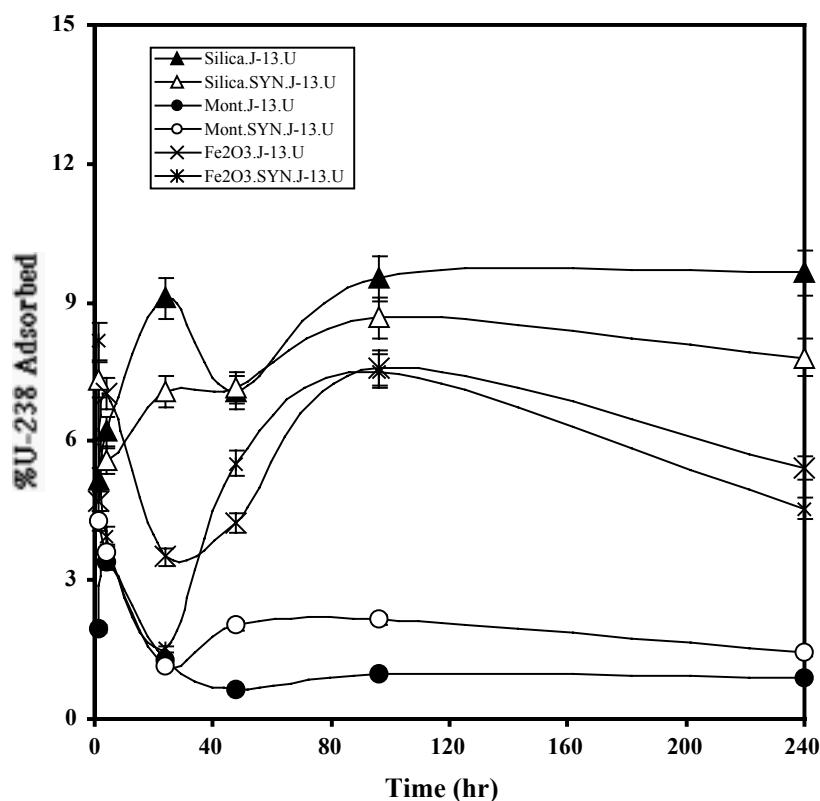




Fig. 4. Percentage of  $^{238}\text{U}$  adsorbed onto colloids of hematite, montmorillonite, and silica as a function of time in natural and synthetic groundwater (colloidal concentration:  $200 \text{ mg L}^{-1}$ )

Very little  $^{238}\text{U}$  was adsorbed by montmorillonite colloids in both natural and synthetic groundwater. Montmorillonite colloids sorbed  $\sim 2\%$  of the  $^{238}\text{U}$  in natural groundwater and  $\sim 4\%$  in synthetic groundwater during the first hour (Fig. 4). In natural groundwater, the amount of the adsorbed  $^{238}\text{U}$  increased to  $\sim 3.6$  at 4 hours, and then it decreased with time for the remaining 236 hours. At the time of maximum adsorption (4 hr), the  $K_d$ -value was  $(1.9 \pm 0.1) \times 10^2 \text{ ml g}^{-1}$  (Table 5). In synthetic groundwater,  $\sim 4.3\%$  of the  $^{238}\text{U}$  was adsorbed onto montmorillonite colloids at 4 hours. Thereafter, the amount of the adsorbed  $^{238}\text{U}$  tended to decrease with time. At the time of maximum adsorption (4 hr), the  $K_d$ -value was  $(2.4 \pm 0.2) \times 10^2 \text{ ml g}^{-1}$  (Table 5).

Table 5. Adsorption distribution coefficients ( $K_d$ -values,  $\text{ml g}^{-1}$ ) of  $^{238}\text{U}$  on colloids of hematite, montmorillonite, and silica as a function of time in natural and synthetic groundwater

Time (hr)	Hematite J-13	Hematite SYN.J-13	Mont. J-13	Mont. SYN.J-13	Silica. J-13	Silica. SYN.J-13
1	$(2.7 \pm 0.6) \times 10^2$	$(4.9 \pm 0.7) \times 10^2$	$(1.1 \pm 0.1) \times 10^2$	$(2.4 \pm 0.2) \times 10^2$	$(2.9 \pm 0.4) \times 10^2$	$(4.3 \pm 0.2) \times 10^2$
4	$(4.1 \pm 0.1) \times 10^2$	$(2.3 \pm 0.05) \times 10^2$	$(1.9 \pm 0.1) \times 10^2$	$(2.1 \pm 0.7) \times 10^2$	$(3.6 \pm 0.3) \times 10^2$	$(3.3 \pm 0.3) \times 10^2$
24	$(2.0 \pm 0.6) \times 10^2$	$(9.0 \pm 1.0) \times 10^1$	$(7.1 \pm 0.6) \times 10^1$	$(6.8 \pm 1.5) \times 10^1$	$(5.7 \pm 0.1) \times 10^2$	$(4.4 \pm 0.2) \times 10^2$
48	$(2.4 \pm 0.8) \times 10^2$	$(3.3 \pm 0.004) \times 10^2$	$(3.5 \pm 0.4) \times 10^1$	$(1.2 \pm 0.02) \times 10^2$	$(4.2 \pm 0.3) \times 10^2$	$(4.3 \pm 0.5) \times 10^2$
96	$(4.4 \pm 0.01) \times 10^2$	$(4.5 \pm 0.2) \times 10^2$	$(5.3 \pm 0.2) \times 10^1$	$(1.2 \pm 0.06) \times 10^2$	$(5.6 \pm 0.05) \times 10^2$	$(5.2 \pm 0.04) \times 10^2$
240	$(3.1 \pm 0.4) \times 10^2$	$(2.7 \pm 0.3) \times 10^2$	$(4.9 \pm 0.4) \times 10^1$	$(8.1 \pm 0.02) \times 10^1$	$(5.8 \pm 0.3) \times 10^2$	$(4.7 \pm 0.3) \times 10^2$

Note: Original data in Table 5 from file "Sorption#4;99-00,U(VI)/Coll., Sorption#4-1;99-00,Time.". The calculation of statistic errors in the Table, referred as to Standard Deviation of Mean, is shown in the file "Np/U.Time.K<sub>d</sub>.Std. Dv.Mean. 99-00".

## Desorption

### Desorption of $^{239}\text{Pu}$

Desorption of  $^{239}\text{Pu}$  from hematite colloids occurred at much lower level than from montmorillonite and silica colloids. After 293 days of desorption, only 0.5% to 0.7% of the adsorbed  $^{239}\text{Pu}$  was desorbed from hematite colloids (Table 6). The  $K_d$ -value of the  $^{239}\text{Pu}$  on the hematite colloids was on the order of  $10^5 \text{ ml g}^{-1}$ . Approximately 21% of the adsorbed  $^{239}\text{Pu}$  was desorbed from the montmorillonite and silica colloids in natural groundwater after 293 days. Approximately 17% of the adsorbed  $^{239}\text{Pu}$  was desorbed from the silica colloids and 20% of the adsorbed  $^{239}\text{Pu}$  was desorbed from the montmorillonite colloids in synthetic groundwater. The  $K_d$ -value of the  $^{239}\text{Pu}$  on both montmorillonite and silica colloids was on the order of  $10^3 \text{ ml g}^{-1}$  after 293 days of desorption (Table 6).

Table 6. Percentages of  $^{239}\text{Pu}$  desorbed and desorption  $K_d$ -values on the colloids of hematite, montmorillonite and silica in natural and synthetic groundwater after 293 days of desorption

Colloids	J-13 water		SYN.J-13 water	
	% Pu desorbed	$K_d$ -value ( $\text{ml g}^{-1}$ )	% Pu desorbed	$K_d$ -value ( $\text{ml g}^{-1}$ )
Hematite	$0.7 \pm 0.02$	$(1.8 \pm 0.1) \times 10^5$	$0.5 \pm 0.003$	$(3.1 \pm 0.1) \times 10^5$
Montmorillonite	$20.9 \pm 0.8$	$(6.9 \pm 0.2) \times 10^3$	$20.2 \pm 1.3$	$(7.3 \pm 0.3) \times 10^3$
Silica	$20.5 \pm 1.3$	$(6.3 \pm 0.5) \times 10^3$	$17.3 \pm 0.2$	$(8.0 \pm 0.1) \times 10^3$

Note: Original data in Table 6 from file "Sorption#1;99-00,Pu/Coll., Sorption#1-2;99-00,Des." The calculation of statistic errors in the Tables, referred as to Standard Deviation of Mean, is shown in the file "Pu/Am.Des.Kd.Std.Dv. Mean. 99-00".

### *Desorption of $^{243}\text{Am}$*

Desorption of  $^{243}\text{Am}$  from hematite colloids was much less than from montmorillonite and silica colloids. After 200 days of desorption,  $\sim 5.8\%$  of the adsorbed  $^{243}\text{Am}$  was desorbed from the hematite colloids in natural groundwater and  $2.9\%$  was desorbed from the hematite colloids in synthetic groundwater. The  $K_d$ -value of the  $^{243}\text{Am}$  on the hematite colloids was  $(1.9 \pm 0.6) \times 10^5 \text{ ml g}^{-1}$  in natural groundwater and  $(8.4 \pm 1.6) \times 10^4 \text{ ml g}^{-1}$  in synthetic groundwater (Table 7). Desorption of  $^{243}\text{Am}$  from montmorillonite colloids was much greater than from hematite colloids. Approximately  $22\%$  of the adsorbed  $^{243}\text{Am}$  in natural groundwater and  $32\%$  of the adsorbed  $^{243}\text{Am}$  in synthetic groundwater were desorbed from the montmorillonite colloids after 200 days of desorption. The  $K_d$ -value of the  $^{243}\text{Am}$  on the montmorillonite colloids was on the order of  $10^4 \text{ ml g}^{-1}$  (Table 7). The amount of the desorbed  $^{243}\text{Am}$  from silica colloids was greater than from hematite and montmorillonite colloids in both natural and synthetic groundwater. About  $26\%$  of the adsorbed  $^{243}\text{Am}$  in natural groundwater and  $\sim 40\%$  of the adsorbed  $^{243}\text{Am}$  in synthetic groundwater were desorbed from the silica

colloids after 200 days. The  $K_d$ -value of  $^{243}\text{Am}$  on the silica colloids was also on the order of  $10^4 \text{ ml g}^{-1}$  (Table 7).

Table 7. Percentage and  $K_d$ -values of  $^{243}\text{Am}$  desorbed from colloids of hematite, montmorillonite and silica in natural and synthetic groundwater after 200 days of desorption

Colloids	J-13 water		SYN.J-13 water	
	% Am desorbed	$K_d$ -value ( $\text{ml g}^{-1}$ )	% Am desorbed	$K_d$ -value ( $\text{ml g}^{-1}$ )
Hematite	$5.8 \pm 0.07$	$(1.9 \pm 0.6) \times 10^5$	$2.9 \pm 0.4$	$(8.4 \pm 1.6) \times 10^4$
Montmorillonite	$21.5 \pm 3.0$	$(9.1 \pm 0.2) \times 10^4$	$31.9 \pm 2.7$	$(1.8 \pm 0.02) \times 10^4$
Silica	$26.3 \pm 1.0$	$(4.6 \pm 0.7) \times 10^4$	$40.1 \pm 0.1$	$(1.0 \pm 0.01) \times 10^4$

Note: Original data in Table 7 from file "Sorption#2;99-00,Am/Coll., Sorption#2-2;99-00,Des." The calculation of statistic errors in the Tables, referred as to Standard Deviation of Mean, is shown in the file "Pu/Am.Des.Kd.Std.Dv. Mean. 99-00".

### *Desorption of $^{237}\text{Np}$ and $^{238}\text{U}$*

After 212 days of desorption, no  $^{237}\text{Np}$  desorbed from hematite colloids, although ~13.5% of the  $^{237}\text{Np}$  in natural groundwater and 28% of the  $^{237}\text{Np}$  in synthetic groundwater were adsorbed onto hematite colloids after 10 days of sorption (Fig. 3). This indicates that hematite colloids hold  $^{237}\text{Np}$  strongly. Because only 0.3% to 1.9% of the  $^{237}\text{Np}$  was adsorbed onto montmorillonite colloids, and only 3% to 9% of the  $^{237}\text{Np}$  was adsorbed onto silica colloids after 240 hours of adsorption (Fig. 3), desorption of the  $^{237}\text{Np}$  from montmorillonite and silica colloids was not observed after the 212 days desorption. It should be mentioned when the colloidal particles were separated from the liquid phase by centrifuging after 240 hours adsorption, ~0.5 ml of the residual solution containing  $^{237}\text{Np}$  tracer remained with the colloid particles. Therefore, a small amount of  $^{237}\text{Np}$  tracer ( $\sim 1 \times 10^{-10} \text{ M}$ ) was left in the residual solution. During 212 days of desorption, no  $^{237}\text{Np}$  desorbed from these three types of colloids,

instead, the residual  $^{237}\text{Np}$  tracer in the solution was slowly adsorbed by these colloids. An additional 1% to 7% of the  $^{237}\text{Np}$  was adsorbed onto hematite colloids, an additional 5% of the  $^{237}\text{Np}$  were adsorbed onto montmorillonite colloids, and an additional 10% of the  $^{237}\text{Np}$  were adsorbed onto silica colloid (data not shown).

Similarly, after 240 hours of adsorption, only 5% of the  $^{238}\text{U}$  was adsorbed onto hematite colloids, 0.9% to 1.4% of the  $^{238}\text{U}$  was adsorbed onto montmorillonite colloids, and 7.8% to 9.6% of the  $^{238}\text{U}$  was adsorbed onto silica colloids (Fig. 3), no  $^{238}\text{U}$  desorbed from any of these three types of colloids after 212 days of desorption. When the colloid particles were separated from the liquid phase by centrifuging after 240 hours of adsorption,  $\sim 0.5$  ml of the residual solution containing  $^{238}\text{U}$  tracer remained with the colloid particles. Therefore, a small amount of the  $^{238}\text{U}$  tracer was left in the residual solution ( $\sim 1 \times 10^{-9}$  M). During 212 days of desorption, no  $^{238}\text{U}$  desorbed from any of these three types of colloids, instead, the residual  $^{238}\text{U}$  tracer in the solution was slowly adsorbed by these colloids. An additional 1% to 6% of the  $^{238}\text{U}$  was sorbed onto colloids of hematite, montmorillonite, and silica during the 212 day desorption period (data not shown).

### Effect of Temperature on Actinide Adsorption

#### *Effect of Temperature on the Adsorption of $^{239}\text{Pu}$ and $^{243}\text{Am}$*

To examine the influence of temperature on the adsorption of the four actinides onto hematite, montmorillonite and silica colloids in natural groundwater, sorption experiments were performed at temperatures of  $20^{\circ}\text{C}$ ,  $40^{\circ}\text{C}$ , and  $80^{\circ}\text{C}$ . Generally, an increase in temperature increased the amount of  $^{239}\text{Pu}$  adsorbed onto these three types of colloids in natural groundwater. As temperature increased from  $20^{\circ}\text{C}$  to  $80^{\circ}\text{C}$ , the amount of  $^{239}\text{Pu}$  adsorbed onto hematite colloids increased by  $\sim 4\%$  and the amount of  $^{239}\text{Pu}$  adsorbed onto silica colloids increased by  $\sim 9\%$  after 10 days of adsorption (Table 8). The  $K_d$ -values of the  $^{239}\text{Pu}$  on the hematite and silica colloids increased by 1 order of magnitude as temperature increased from

20°C to 80°C (Table 8). Temperature greatly affected the adsorption of  $^{239}\text{Pu}$  by montmorillonite colloids. As temperature increased from 20°C to 80°C, the amount of  $^{239}\text{Pu}$  adsorbed onto montmorillonite colloids increased from 58% to 97% in natural groundwater after 10 day of adsorption. The  $K_d$ -values of the  $^{239}\text{Pu}$  on the montmorillonite colloids increased by 2 orders of magnitude as temperature increased (Table 8)

Table 8. The percentage of  $^{239}\text{Pu}$  adsorbed and the adsorption  $K_d$ -values of  $^{239}\text{Pu}$  on colloids of hematite, montmorillonite and silica as a function of temperature in natural groundwater after 10 days of sorption.

Colloid	20°C		40°C		80°C	
	% Pu Adsorbed	$K_d$ (ml g <sup>-1</sup> )	% Pu Adsorbed	$K_d$ (ml g <sup>-1</sup> )	% Pu Adsorbed	$K_d$ (ml g <sup>-1</sup> )
Hematite	96.1±0.07	(1.7±0.03) × 10 <sup>5</sup>	99.3±0.02	(1.0±0.03) × 10 <sup>6</sup>	99.9±0.03	(4.9±0.9) × 10 <sup>6</sup>
Montmorillonite	58.4±0.3	(9.5±0.1) × 10 <sup>3</sup>	65.4±0.07	(1.0±0.01) × 10 <sup>4</sup>	96.5±0.03	(2.0±0.02) × 10 <sup>5</sup>
Silica	56.5±0.1	(8.8±0.05) × 10 <sup>3</sup>	59.8±0.5	(1.1±0.02) × 10 <sup>4</sup>	62.1±0.4	(1.2±0.02) × 10 <sup>4</sup>

Note: Original data in Table 8 from file "Sorption#1;99-00,Pu(V)/Coll., Sorption#1-4;99-00,Temp." The calculation of statistic errors in the Table, referred as to Standard Deviation of Mean, is shown in the file "Pu/Am.Temp.Kd. Std.Dv.Mean.00".

Temperature slightly influenced the adsorption of  $^{243}\text{Am}$  onto colloids of hematite, montmorillonite, and silica. As temperature increased from 20°C to 80°C, the amount of  $^{243}\text{Am}$  adsorbed onto these three types of colloids increased by only ~3.6% onto hematite, by ~11% onto montmorillonite, and by ~9% onto silica after 10 days of sorption (Table 9). The  $K_d$ -values of the  $^{243}\text{Am}$  on the three types of colloids were on the order of 10<sup>5</sup> ml g<sup>-1</sup> for the hematite and montmorillonite colloids and on the order of 10<sup>4</sup> ml g<sup>-1</sup> for the silica colloids at 80°C.

#### *Effect of Temperature on the Sorption of $^{237}\text{Np}$ and $^{238}\text{U}$*

Generally, temperature significantly influenced the adsorption of  $^{237}\text{Np}$  onto colloids of

hematite, montmorillonite, and silica in natural groundwater. As temperature increased from 20°C to 80°C, the amount of  $^{237}\text{Np}$  adsorbed onto hematite increased from ~11% to ~38% after 10 days of the sorption. The  $K_d$ -values of the  $^{237}\text{Np}$  on the hematite colloids increased by ~6 times as temperature increased from 20°C to 80°C (Table 10). Temperature also greatly affected the adsorption of  $^{237}\text{Np}$  onto montmorillonite colloids. As temperature increased from 20°C to 80°C, the amount of  $^{237}\text{Np}$  adsorbed onto montmorillonite colloids increased from ~2% to ~28% after 10 days of sorption. The  $K_d$ -values of the  $^{237}\text{Np}$  on the montmorillonite colloids increased by ~1 order of magnitude as temperature increased from 20°C to 80°C (Table 10). Adsorption of  $^{243}\text{Am}$  on colloids of hematite, montmorillonite and silica as a function of temperature in natural groundwater after 10 days of sorption.

Colloid	20°C		40°C		80°C	
	% Am Adsorbed	$K_d$ (ml g <sup>-1</sup> )	%Am Adsorbed	$K_d$ (ml g <sup>-1</sup> )	% Am Adsorbed	$K_d$ (ml g <sup>-1</sup> )
Hematite	95.3±0.3	(1.8±0.1)x 10 <sup>5</sup>	95.9±0.03	(2.0±0.02) x10 <sup>5</sup>	98.7±0.09	(6.5±0.4)x 10 <sup>5</sup>
Montmorillonite	87.1±0.4	(6.0±0.2)x 10 <sup>4</sup>	89.8±0.1	(7.7±0.1)x 10 <sup>4</sup>	96.8±0.2	(2.7±0.1)x 10 <sup>5</sup>
Silica	79.3±0.4	(2.9±0.3)x 10 <sup>4</sup>	81.3±0.6	(3.8±0.1)x 10 <sup>4</sup>	86.5±0.4	(6.2±1.5)x 10 <sup>4</sup>

Note: Original data in Table 9 from file "Sorption#2;99-00, Am/Coll., Sorption#2-4;99-00,Temp." The calculation of statistic errors in the Table, referred as to Standard Deviation of Mean, is shown in the file "Pu/Am. Temp.Kd. Std.Dv.Mean,99-00".

$^{237}\text{Np}$  onto silica colloids was 4.5 times higher at 80°C than at 20°C. The  $K_d$ -values of the  $^{237}\text{Np}$  on the silica colloids also increased by 1 order of magnitude as temperature increased from 20°C to 80°C (Table 10).

Temperature only slightly influenced the adsorption of  $^{238}\text{U}$  onto hematite colloids, but it significantly affected the adsorption of  $^{238}\text{U}$  onto montmorillonite and silica colloids. As temperature increased from 20°C to 80°C, the amount of  $^{238}\text{U}$  adsorbed onto hematite increased

by only 2 times and the  $K_d$ -values of the  $^{238}\text{U}$  were still on the order of  $10^2 \text{ ml g}^{-1}$  (Table 11). As temperature increased from  $20^\circ\text{C}$  to  $80^\circ\text{C}$ , the amount of  $^{238}\text{U}$  adsorbed onto montmorillonite increased by  $\sim 5$  times and the  $K_d$ -values of the  $^{238}\text{U}$  increased by  $\sim 4.5$  times (Table 11). As temperature increased from  $20^\circ\text{C}$  to  $80^\circ\text{C}$ , the amount of  $^{238}\text{U}$  adsorbed onto montmorillonite increased by  $\sim 2.5$  times, and the  $K_d$ -values of the  $^{238}\text{U}$  increased by  $\sim 3$  times (Table 11).

### Effect of Ionic Strength on Actinides Adsorption

#### *Effect of Ionic Strength on the Adsorption of $^{239}\text{Pu}$ and $^{243}\text{Am}$*

Based on the chemical composition of J-13 water, four synthetic J-13 waters with different ionic strengths were used to examine the influence of ionic strength on the adsorption of the four actinides onto colloids of hematite, montmorillonite, and silica at room temperature.

Table 10. The percentage of  $^{237}\text{Np}$  adsorbed and the adsorption  $K_d$ -values of  $^{237}\text{Np}$  on colloids of

hematite, montmorillonite and silica as a function of temperature in natural groundwater after 10 days of sorption.

Colloid	$20^\circ\text{C}$		$40^\circ\text{C}$		$80^\circ\text{C}$	
	%Np Adsorbed	$K_d$ ( $\text{ml g}^{-1}$ )	%Np Adsorbed	$K_d$ ( $\text{ml g}^{-1}$ )	%Np Adsorbed	$K_d$ ( $\text{ml g}^{-1}$ )
Hematite	$10.5 \pm 0.3$	$(7.1 \pm 0.3) \times 10^2$	$28.4 \pm 0.6$	$(2.6 \pm 0.1) \times 10^3$	$37.6 \pm 4.0$	$(4.1 \pm 0.7) \times 10^3$
Montmorillonite	$2.3 \pm 0.5$	$(1.5 \pm 0.3) \times 10^2$	$13.0 \pm 0.02$	$(9.8 \pm 0.02) \times 10^2$	$28.2 \pm 3.3$	$(2.7 \pm 0.4) \times 10^3$
Silica	$4.1 \pm 0.1$	$(2.6 \pm 0.08) \times 10^2$	$9.8 \pm 1.0$	$(7.1 \pm 0.8) \times 10^2$	$18.7 \pm 0.4$	$(1.6 \pm 0.06) \times 10^3$

Note: Original data in Table 10 from file "Sorption#3;99-00, Np/Coll., Sorption#3-2;99-00, Temp." The calculation of statistic errors in the Table, referred as to Standard Deviation of Mean, is shown in the file "Np/U.Temp.Kd.Std.Dv.Mean.00".



The ionic strengths of the solutions were adjusted to  $4.7 \times 10^{-3}$ ,  $1.7 \times 10^{-2}$ ,  $7.1 \times 10^{-2}$ , and  $1.34 \times 10^{-1}$  M. Generally, ionic strength differences had only slight influence on the adsorption of  $^{239}\text{Pu}$  and  $^{243}\text{Am}$  onto hematite colloids, but it greatly affected the adsorption of  $^{239}\text{Pu}$  and  $^{243}\text{Am}$  onto montmorillonite and silica colloids. As the ionic strength increased, the amount of  $^{239}\text{Pu}$  adsorbed onto hematite colloids increased from ~93% to 100% (Fig. 5). The  $K_d$ -values of the  $^{239}\text{Pu}$  on the hematite increased by a factor of 10 to 100 over the range of ionic strength (Table 12). As the ionic strength increased, the amount of  $^{243}\text{Am}$  adsorbed by the hematite colloids decreased from 99% to 94% (Fig. 6), but the  $K_d$ -values of the  $^{243}\text{Am}$  on the hematite colloids were still on the order of  $10^5 \text{ ml g}^{-1}$  (Table. 13). In the case of montmorillonite colloids, as the ionic strength increased, the amount of adsorbed  $^{239}\text{Pu}$  tended to decrease to where only ~41% of  $^{239}\text{Pu}$  was adsorbed at an ionic strength of 0.134 M (Fig. 6). The  $K_d$ -value of the  $^{239}\text{Pu}$  on the montmorillonite colloids was  $\sim 10^3 \text{ ml g}^{-1}$  (Table 12). As the ionic strength increased, the amount of  $^{243}\text{Am}$  adsorbed on the montmorillonite colloids decreased from ~91% to ~54%. The  $K_d$ -values of the  $^{243}\text{Am}$  on the montmorillonite colloids decreased by ~10 times over the range of ionic strengths (Table. 13). In the case of silica colloids, as the ionic strength increased, the amount of adsorbed  $^{239}\text{Pu}$  tended to decrease and only ~41% of the  $^{239}\text{Pu}$  was adsorbed at an ionic strength of 0.134 M (Fig. 6). The  $K_d$ -value of the  $^{239}\text{Pu}$  on the silica colloids was  $\sim 10^3 \text{ ml g}^{-1}$  (Table 12). As the ionic strength increased, the amount of  $^{243}\text{Am}$  adsorbed on the silica colloids decreased from ~91% to ~54%. The  $K_d$ -values of the  $^{243}\text{Am}$  on the silica colloids decreased by ~10 times over the range of ionic strengths (Table. 13).

Table 11. The percentage of  $^{238}\text{U}$  adsorbed and the adsorption  $K_d$ -values of  $^{238}\text{U}$  on colloids of hematite, montmorillonite and silica as a function of temperature in natural groundwater after 10 days of sorption.

Colloid	20°C		40°C		80°C	
	% U Adsorbed	$K_d$ ( $\text{ml g}^{-1}$ )	%U Adsorbed	$K_d$ ( $\text{ml g}^{-1}$ )	% U Adsorbed	$K_d$ ( $\text{ml g}^{-1}$ )
Hematite	$4.7 \pm 0.004$	$(2.8 \pm 0.01) \times 10^2$	$5.3 \pm 0.7$	$(3.3 \pm 0.4) \times 10^2$	$7.8 \pm 0.7$	$(5.0 \pm 0.5) \times 10^2$
Montmorillonite	$2.6 \pm 0.9$	$(1.5 \pm 0.5) \times 10^2$	$10.5 \pm 0.3$	$(7.0 \pm 0.4) \times 10^2$	$10.5 \pm 0.7$	$(6.9 \pm 0.5) \times 10^2$

Silica	$9.5 \pm 0.6$	$(5.8 \pm 0.4) \times 10^2$	$22.3 \pm 0.7$	$(1.7 \pm 0.07) \times 10^3$	$23.4 \pm 0.4$	$(1.8 \pm 0.06) \times 10^3$
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Note: Original data in Table 11 from file "Sorption#4;99-00, U/Coll., Sorption#4-2;99-00,Temp." The calculation of statistic errors in the Table, referred as to Standard Deviation of Mean, is shown in the file "Np/U.Temp.Kd.Std.Dv.Mean.00".

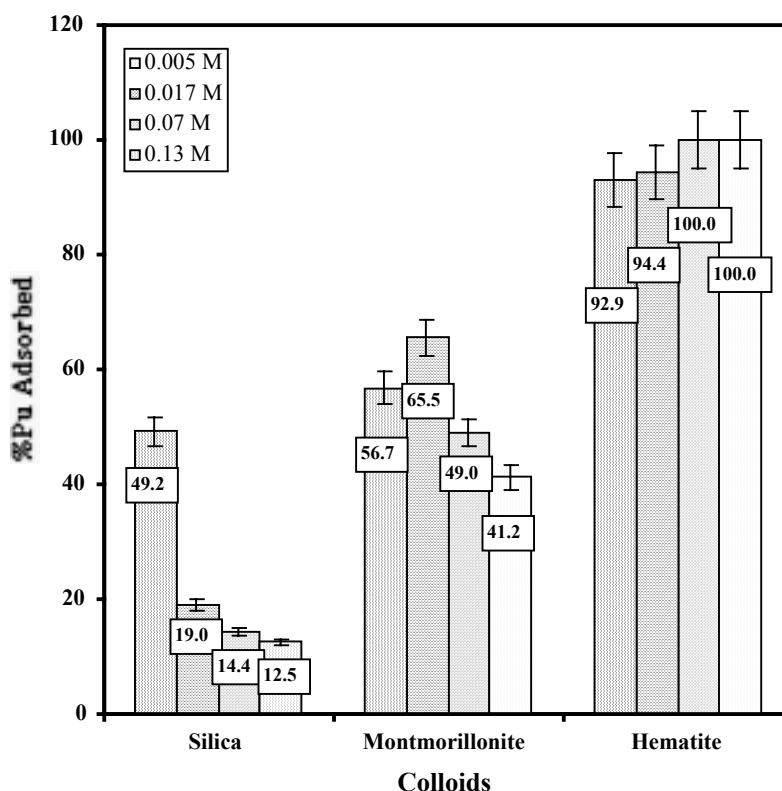


Fig. 5. Adsorption of  $^{239}\text{Pu}$  onto colloids of hematite, montmorillonite, and silica as a function of ionic strength in synthetic J-13 groundwaters after 10 days of sorption

Table 12. The  $K_d$ -values ( $\text{ml g}^{-1}$ ) of the  $^{239}\text{Pu}$  on colloids of hematite, montmorillonite, and silica as a function of ionic strength in synthetic groundwaters after 10 days of sorption

Ionic Strength M	Hematite $K_d$ ( $\text{ml g}^{-1}$ )	Montmorillonite $K_d$ ( $\text{ml g}^{-1}$ )	Silica $K_d$ ( $\text{ml g}^{-1}$ )
0.005	$(7.4 \pm 0.04) \times 10^4$	$(7.3 \pm 0.3) \times 10^3$	$(5.4 \pm 0.1) \times 10^3$
0.017	$(1.4 \pm 0.6) \times 10^5$	$(1.2 \pm 0.3) \times 10^4$	$(1.3 \pm 0.02) \times 10^3$
0.071	$(1.0 \pm 0.0) \times 10^7$	$(5.9 \pm 1.5) \times 10^3$	$(9.9 \pm 0.9) \times 10^2$

0.134	$(1.2 \pm 0.1) \times 10^7$	$(4.0 \pm 0.3) \times 10^3$	$(8.3 \pm 1.4) \times 10^2$
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Note: Original data in Table 12 from file "Sorption#1;99-00, Pu/Coll., Sorption#1-5;99-00, Ion." The calculation of statistic errors in the Table, referred as to Standard Deviation of Mean, is shown in the file "Pu/Am.IonicStr.Kd.Std.Dv.Mean,99-00".

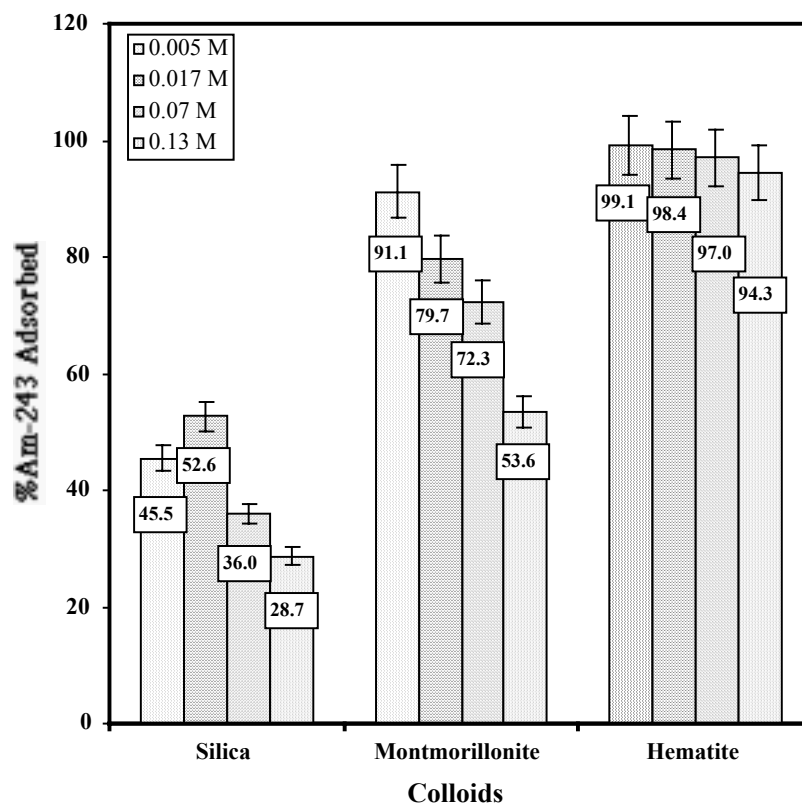


Fig. 6. Adsorption of  $^{243}\text{Am}$  onto colloids of hematite, montmorillonite, and silica as a function of ionic strength in synthetic J-13 groundwaters after 10 days of sorption

Table 13. The  $K_d$ -values ( $\text{ml g}^{-1}$ ) of the  $^{243}\text{Am}$  on colloids of hematite, montmorillonite, and silica as a function of ionic strength in synthetic groundwaters after 10 days of sorption

Ionic Strength M	Hematite $K_d$ ( $\text{ml g}^{-1}$ )	Montmorillonite $K_d$ ( $\text{ml g}^{-1}$ )	Silica $K_d$ ( $\text{ml g}^{-1}$ )
0.005	$(8.5 \pm 1.5) \times 10^5$	$(7.5 \pm 0.8) \times 10^4$	$(6.0 \pm 0.05) \times 10^3$
0.017	$(4.2 \pm 0.5) \times 10^5$	$(2.7 \pm 0.03) \times 10^4$	$(7.6 \pm 0.2) \times 10^3$

0.071	$(2.5 \pm 0.5) \times 10^5$	$(1.9 \pm 0.3) \times 10^4$	$(3.9 \pm 0.1) \times 10^3$
0.134	$(1.2 \pm 0.02) \times 10^5$	$(8.3 \pm 0.03) \times 10^3$	$(2.9 \pm 0.05) \times 10^3$

Note: Original data in Table 13 from file "Sorption#2;99-00, Am/Coll., Sorption#2-5;99-00, Ion." The calculation of statistic errors in the Table, referred as to Standard Deviation of Mean, is shown in the file "Pu/Am.IonicStr.Kd.Std.Dv.Mean,99-00".

ionic strength of 0.134 M (Fig. 5). The  $K_d$ -value of the  $^{239}\text{Pu}$  on the silica colloids decreased by  $\sim 10$  times over the range of ionic strengths (Table 12). As the ionic strength increased, the amount of adsorbed  $^{243}\text{Am}$  tended to decrease, and only  $\sim 29\%$  of the  $^{243}\text{Am}$  was adsorbed at an ionic strength of 0.134 M (Fig. 6). The  $K_d$ -values of the  $^{243}\text{Am}$  on the silica colloids decreased by 2 times over the range of ionic strength (Table 13).

#### *Effect of Ionic Strength on the Adsorption of $^{237}\text{Np}$ and $^{238}\text{U}$*

Generally, ionic strength did not significantly influence the adsorption of  $^{237}\text{Np}$  by hematite and montmorillonite colloids, but did affect the adsorption of  $^{237}\text{Np}$  by silica colloids. As the ionic strength increased, the amount of  $^{237}\text{Np}$  adsorbed onto hematite and montmorillonite colloids did not change much (Table 14). The  $K_d$ -values of the  $^{237}\text{Np}$  on the hematite and montmorillonite colloids were still on the order of  $\sim 10^2 \text{ ml g}^{-1}$  (Table 14). As the ionic strength increased, the amount of  $^{237}\text{Np}$  adsorbed onto silica colloids decreased from  $\sim 21\%$  to  $\sim 3\%$ , and the  $K_d$ -values of the  $^{237}\text{Np}$  on the silica colloids decreased by a factor of 10 over the range of ionic strengths (Table. 14).

The ionic strength significantly influenced the solubility of  $^{238}\text{U}$  (Fig. 7). As the ionic strength increased, the solubility of the  $^{238}\text{U}$  decreased, resulting in co-precipitation of  $^{238}\text{U}$  with  $\text{CaCO}_3$  at the ionic strengths of 0.071 M and 0.134 M. From control samples with colloid-free Table 14. The percentage of  $^{237}\text{Np}$  adsorbed onto colloids of hematite, montmorillonite, and silica as a function of ionic strength in synthetic groundwaters after 10 days of sorption

Ionic Strength M		Hematite	Montmorillonite	Silica
0.005	%Np adsorbed $K_d$ -values (ml g <sup>-1</sup> )	6.0±2.9 (3.5±0.4) x 10 <sup>2</sup>	2.1±2.9 (1.2±0.5) x 10 <sup>2</sup>	20.7±1.0 (1.4±0.08) x 10 <sup>3</sup>
0.017	%Np adsorbed $K_d$ -values (ml g <sup>-1</sup> )	7.6±0.5 (4.6±0.3) x 10 <sup>2</sup>	1.9±0.5 (1.1±0.3) x 10 <sup>2</sup>	8.0±3.7 (5.0±2.4) x 10 <sup>2</sup>
0.071	%Np adsorbed $K_d$ -values (ml g <sup>-1</sup> )	10.8±3.4 (7.1±2.5) x 10 <sup>2</sup>	2.2±0.3 (1.3±0.2) x 10 <sup>2</sup>	7.3±2.4 (4.6±1.6) x 10 <sup>2</sup>
0.134	%Np adsorbed $K_d$ -values (ml g <sup>-1</sup> )	8.2±1.8 (5.4±1.3) x 10 <sup>2</sup>	1.3±0.07 (7.7±0.4) x 10 <sup>1</sup>	2.9±2.1 (1.8±1.3) x 10 <sup>2</sup>

Note: Original data in Table 14 from file "Sorption#3;99-00, Np/Coll., Sorption#3-3;99-00, Ion." The calculation of statistic errors in the Table, referred as to Standard Deviation of Mean, is shown in the file "Np/U.IonicStr.Std.Dv. Mean,99-00"

solutions, ~40% of the <sup>238</sup>U was co-precipitated at an ionic strength of 0.071 M and 100% of the <sup>238</sup>U was co-precipitated at an ionic strength of 0.134 M (Fig.7). These results are misleading, making it appear as if 100% of the <sup>238</sup>U was adsorbed by these three types of colloids at an ionic strength of 0.134 M (Table 15), with corresponding  $K_d$ -values of 10<sup>7</sup> ml g<sup>-1</sup> (Table 15).

### Effect of Colloid Concentration on the Adsorption of <sup>239</sup>Pu and <sup>243</sup>Am

To examine the influence of colloid concentration on the adsorption of <sup>239</sup>Pu(V) and <sup>243</sup>Am(III), experiments were conducted at room temperature in natural and synthetic groundwater with an ionic strength of 0.005 M. The colloid concentrations were 10, 50, 100,

150, 200, and 1000 mg L<sup>-1</sup>. Adsorption of <sup>239</sup>Pu and <sup>243</sup>Am per unit mass of colloid was much higher at low colloid concentrations than that at high colloid concentrations in both natural and

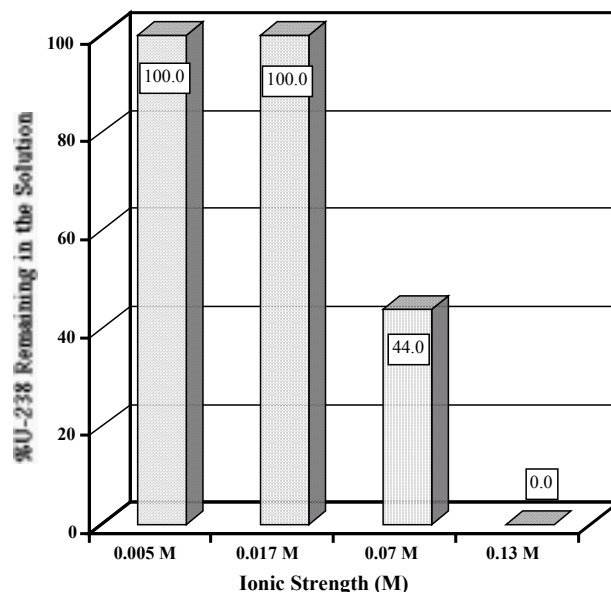


Fig. 7. Effect of ionic strength on the solubility of <sup>238</sup>U in synthetic J-13 groundwaters

synthetic groundwater (Table 16, 17). In natural groundwater, at 10 mg L<sup>-1</sup>, hematite colloids sorbed 27 times more <sup>239</sup>Pu and 100 times more <sup>243</sup>Am than at 1000 mg L<sup>-1</sup>. The montmorillonite colloids sorbed 25 times more <sup>239</sup>Pu and 92 times more <sup>243</sup>Am at 10 mg L<sup>-1</sup> than at 1000 mg L<sup>-1</sup>. The silica colloids sorbed 47 times more <sup>239</sup>Pu and 89 times more <sup>243</sup>Am at 10 mg L<sup>-1</sup> than at 1000 mg L<sup>-1</sup> (Table 16 and Table 17). At low colloid concentrations of 10 and 50 mg L<sup>-1</sup>, the K<sub>d</sub>-values of the <sup>239</sup>Pu were on the order of 10<sup>4</sup> ml g<sup>-1</sup> for hematite and montmorillonite colloids and on the orders of 10<sup>3</sup> to 10<sup>4</sup> ml g<sup>-1</sup> for silica colloids (Table 16). At a colloid concentration of 1000 mg L<sup>-1</sup>, the K<sub>d</sub>-values of the <sup>239</sup>Pu were 10<sup>4</sup> ml g<sup>-1</sup> for hematite colloids, 10<sup>3</sup> ml g<sup>-1</sup> for montmorillonite colloids, and 10<sup>2</sup> ml g<sup>-1</sup> for silica colloids.

At the low colloid concentrations of 10 to 50 mg L<sup>-1</sup>, the K<sub>d</sub>-values for <sup>243</sup>Am were on the order of 10<sup>6</sup> to 10<sup>7</sup> ml g<sup>-1</sup> for hematite colloids, on the order of 10<sup>5</sup> to 10<sup>6</sup> ml g<sup>-1</sup> for montmorillonite colloids, and on the order of 10<sup>4</sup> to 10<sup>6</sup> ml g<sup>-1</sup> for silica colloids (Table 17). At 1000 mg L<sup>-1</sup>, the K<sub>d</sub>-values of <sup>243</sup>Am were on the order of 10<sup>4</sup> ml g<sup>-1</sup> for all three types of colloids. In synthetic groundwater, adsorption experiments with <sup>239</sup>Pu and <sup>243</sup>Am showed similar results. Table 15. The percentage of <sup>238</sup>U adsorbed onto colloids of hematite, montmorillonite, and silica as a function of ionic strength in synthetic J-13 groundwaters after 10 days of sorption

Ionic Strength M		Hematite	Montmorillonite	Silica
0.005	%U adsorbed K <sub>d</sub> -values (ml g <sup>-1</sup> )	4.4±0.6 (2.4±0.4) x 10 <sup>2</sup>	7.4±1.5 (4.2±0.1) x 10 <sup>2</sup>	12.2±0.1 (7.3±0.07) x 10 <sup>2</sup>
0.017	%U adsorbed K <sub>d</sub> -values (ml g <sup>-1</sup> )	7.8±0.3 (4.3±0.2) x 10 <sup>2</sup>	12.8±0.7 (7.6±0.5) x 10 <sup>2</sup>	10.1±0.9 (5.8±0.6) x 10 <sup>2</sup>
0.071	%U adsorbed K <sub>d</sub> -values (ml g <sup>-1</sup> )	21.5±4.4 (2.2±0.5) x 10 <sup>3</sup>	99.9±0.01 *(1.2±0.2) x 10 <sup>7</sup>	17.0±0.4 (1.6±0.04) x 10 <sup>3</sup>
0.134	%U adsorbed K <sub>d</sub> -values (ml g <sup>-1</sup> )	100±0.0 *(3.3±0.01) x 10 <sup>7</sup>	100±0.0 *(3.3±0.06) x 10 <sup>7</sup>	100±0.0 *(3.8±0.2) x 10 <sup>7</sup>

Note: Original data in Table 14 from file "Sorption#4;99-00, U/Coll., Sorption#4-3;99-00, Ion." The calculation of statistic errors in the Table, referred as to Standard Deviation of Mean, is shown in the file "Np/U.IonicStr.Std.Dv. Mean,99-00"

\* Co-precipitation of <sup>238</sup>U(VI) with CaCO<sub>3</sub> was observed in the control samples. Thus, the K<sub>d</sub>-values obtained at ionic strengths of 0.07 M and 0.13 M are not the true adsorption K<sub>d</sub> because of co-precipitation of <sup>238</sup>U with CaCO<sub>3</sub>.

results in natural groundwater (data not shown). The K<sub>d</sub>-values were probably lower at the higher colloid concentrations than at the lower colloid concentrations, because colloid aggregation may

occur at higher colloid concentrations, resulting in less surface area per unit mass of colloids at the higher concentrations.

## DISCUSSION

We generally observed that the amount of  $^{239}\text{Pu}$ ,  $^{243}\text{Am}$ ,  $^{237}\text{Np}$  and  $^{238}\text{U}$  adsorbed onto colloids of hematite, montmorillonite, and silica in natural groundwater was lower than in synthetic groundwater. These three types of colloids may sorb dissolved organic carbon that is present in natural groundwater (1.0 ppm of TOC), resulting in less  $^{239}\text{Pu}$ ,  $^{243}\text{Am}$ ,  $^{237}\text{Np}$  and  $^{238}\text{U}$  being adsorbed. The presence of multivalent cations in natural groundwater may also influence

Table 16. The amounts (pCi/mg) of the  $^{239}\text{Pu}$  adsorbed and the  $K_d$ -values ( $\text{ml g}^{-1}$ ) onto colloids of hematite, montmorillonite, and silica as a function of colloid concentration in natural groundwater after 10 days of sorption

Colloid Conc., ( $\text{mg L}^{-1}$ )		Hematite J-13	Montmorillonite J-13	Silica J-13
10	Pu adsorbed (pCi/mg) $K_d$ -values ( $\text{ml g}^{-1}$ )	2910.6±90.7 (3.7±0.1) × 10 <sup>4</sup>	2264.2±21.5 (2.7±0.08) × 10 <sup>4</sup>	2516.6±6.8 (3.0±0.02) × 10 <sup>4</sup>
50	Pu adsorbed (pCi/mg) $K_d$ -values ( $\text{ml g}^{-1}$ )	1362.2±18.2 (3.2±0.06) × 10 <sup>4</sup>	1113.6±23.1 (2.3±0.01) × 10 <sup>4</sup>	548.2±14.3 (6.8±0.2) × 10 <sup>3</sup>
100	Pu adsorbed (pCi/mg) $K_d$ -values ( $\text{ml g}^{-1}$ )	461.0±28.0 (7.5±0.7) × 10 <sup>3</sup>	654.3±14.9 (1.4±0.04) × 10 <sup>4</sup>	319.0±1.3 (4.2±0.03) × 10 <sup>3</sup>
150	Pu adsorbed (pCi/mg) $K_d$ -values ( $\text{ml g}^{-1}$ )	465.1±0.3 (1.2±0.04) × 10 <sup>4</sup>	334.1±14.2 (5.3±0.3) × 10 <sup>3</sup>	232.4±1.9 (3.2±0.03) × 10 <sup>3</sup>
200	Pu adsorbed (pCi/mg)	436.7±17.1	243.8±5.2	231.2±3.4



	$K_d$ -values (ml g <sup>-1</sup> )	$(1.8 \pm 0.3) \times 10^4$	$(3.9 \pm 0.1) \times 10^3$	$(3.6 \pm 0.1) \times 10^3$
1000	Pu adsorbed (pCi/mg)	106.6 ± 0.5	92.1 ± 0.5	52.9 ± 0.6
	$K_d$ -values (ml g <sup>-1</sup> )	$(1.3 \pm 0.09) \times 10^4$	$(4.2 \pm 0.2) \times 10^3$	$(8.7 \pm 0.4) \times 10^2$

Note: Original data in Table 16 from file "Sorption#1;99-00, Pu/Coll., Sorption#1-3;99-00, Conc." The calculation of statistic errors in the Table, referred as to Standard Deviation of Mean, is shown in the file "Pu/Am.Conc.Str.Kd.Std.Dv.Mean,99-00".

the adsorption of the four actinides. The pH of the waters tended to decrease by 0.5 to 1 unit during the experiments, probably as a result of the actinides reacting with hydroxyl groups on the colloid surface.

The primary surface functional group of hematite is FeOH. The pH of PZNPC (point of zero net proton charge) for hematite is 4.2 (Langmuir, 1997). With a solution pH of 8.2 to 8.4 some FeOH groups may be deprotonated to FeO<sup>-</sup>. Therefore, sites of ≡FeOH, and ≡FeO<sup>-</sup> may

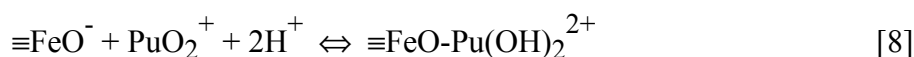
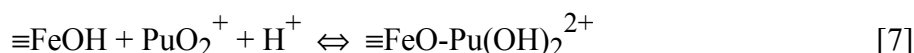
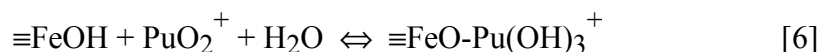
Table 17. Amount (pCi/mg) of <sup>243</sup>Am adsorbed and the  $K_d$ -values (ml g<sup>-1</sup>) onto colloids of hematite, montmorillonite, and silica as a function of colloid concentrations in natural groundwater after 10 days of sorption

Colloid Conc, (mg L <sup>-1</sup> )		Hematite J-13	Montmorillonite J-13	Silica J-13
10	Am adsorbed (pCi/mg)	1518.7 ± 1.1	1382.4 ± 18.2	1341.0 ± 7.6
	$K_d$ -values (ml g <sup>-1</sup> )	$(1.6 \pm 1.1) \times 10^7$	$(1.5 \pm 0.2) \times 10^6$	$(1.3 \pm 0.03) \times 10^6$
50	Am adsorbed (pCi/mg)	306.5 ± 2.2	263.4 ± 16.1	222.3 ± 20.1
	$K_d$ -values (ml g <sup>-1</sup> )	$(9.0 \pm 2.0) \times 10^6$	$(2.5 \pm 1.0) \times 10^5$	$(7.8 \pm 0.9) \times 10^4$
100	Am adsorbed (pCi/mg)	151.1 ± 0.3	150.9 ± 0.03	121.9 ± 0.8
	$K_d$ -values (ml g <sup>-1</sup> )	$(1.9 \pm 0.2) \times 10^6$	$(8.8 \pm 0.6) \times 10^5$	$(6.5 \pm 0.2) \times 10^4$
150	Am adsorbed (pCi/mg)	101.8 ± 0.2	95.9 ± 0.1	75.6 ± 0.4

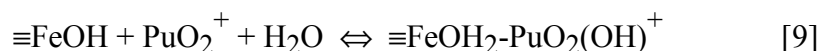
	$K_d$ -values (ml g <sup>-1</sup> )	$(2.5 \pm 0.6) \times 10^6$	$(1.6 \pm 0.04) \times 10^5$	$(3.2 \pm 0.01) \times 10^4$
200	Am adsorbed (pCi/mg) $K_d$ -values (ml g <sup>-1</sup> )	$76.8 \pm 0.2$ $(3.4 \pm 0.008) \times 10^6$	$74.3 \pm 0.6$ $(1.8 \pm 0.2) \times 10^4$	$63.7 \pm 1.5$ $(3.9 \pm 0.5) \times 10^4$
1000	Am adsorbed (pCi/mg) $K_d$ -values (ml g <sup>-1</sup> )	$14.8 \pm 0.08$ $(3.5 \pm 0.3) \times 10^4$	$14.7 \pm 0.02$ $(3.5 \pm 0.2) \times 10^4$	$15.1 \pm 1.0$ $(2.2 \pm 0.6) \times 10^4$

Note: Original data in Table 17 from file "Sorption#2;99-00, Am/Coll., Sorption#2-3;99-00, Conc.." The calculation of statistic errors in the Table, referred as to Standard Deviation of Mean, is shown in the file "Pu/Am.conc.Str.Kd. Std. Dv.Mean,99-00" —Attachment #3 for Kd Tables;99-00.

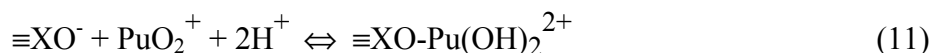
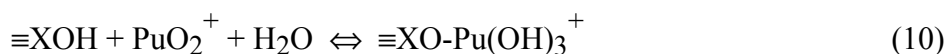
exist on the surface of hematite colloids. Adsorption of <sup>239</sup>Pu, <sup>243</sup>Am, <sup>237</sup>Np and <sup>238</sup>U may be the result of a complexation process, in which these actinides bind to OH<sup>-</sup> groups on the surface of hematite colloids. In the following discussion, we use Pu(V) as an example to discuss the surface complexation. In both natural and synthetic groundwaters, Pu(V) exists as its PuO<sub>2</sub><sup>+</sup> form. Adsorption of PuO<sub>2</sub><sup>+</sup> onto iron oxide colloids can be chemically described by the following reaction(s):



The complexes of  $\equiv\text{FeO-Pu(OH)}_2^{2+}$  and  $\equiv\text{FeO-Pu(OH)}_3^+$  may be formed. However, the hydrolysis constants for adsorption of Pu(V) onto iron oxides are not well known (Sanchez, *et al.*, 1985). The fact that the pH tended to decrease during the sorption experiments suggests that it is more likely that reaction [6] occurred in our experiments than reaction [7] or [8]. It is also possible that another reaction, such as that suggested by Langmuir (1997), occurred:



Two types of charged sites exist on the surfaces of the montmorillonite colloids. The first of these are fixed charge sites, which are caused by the isomorphic substitution of trivalent ions in the octahedral sheets of the structure of montmorillonite with bivalent ions such as  $\text{Fe}^{2+}$  and  $\text{Mg}^{2+}$  (Gast, 1977). This process results in a net negative charge and does not change with the solution pH. The other type of charged site is a pH-dependent site. The primary pH-dependent sites are at the edges of the montmorillonite platelets and include aluminol ( $\text{AlOH}$ ) and silanol ( $\text{SiOH}$ ) groups (Langmuir, 1997). These aluminol and silanol sites may account for 30% to 40% of the external surface area of montmorillonite. With a solution pH of  $\sim 8.5$ , some  $\text{AlOH}$  and  $\text{SiOH}$  groups may be deprotonated to  $\text{AlO}^-$  and  $\text{SiO}^-$ , respectively, because of the low pH of PZNPC ( $\leq 2$  to 3) for montmorillonite (Langmuir, 1997). Assuming that  $\text{PuO}_2^+$  binding to these sites is analogous to aqueous coordination reactions, the adsorption of  $\text{PuO}_2^+$  onto montmorillonite colloids could be described by the following reactions (Liang and McCarthy, 1995):



where  $\text{X} = \text{Al}$  or  $\text{Si}$ . Thus, complexes of  $\equiv\text{AlO-Pu(OH)}_3^+$ ,  $\equiv\text{AlO-Pu(OH)}_2^{2+}$ ,  $\equiv\text{SiO-Pu(OH)}_3^+$ , and  $\equiv\text{SiO-Pu(OH)}_2^{2+}$  may be formed on the surfaces of montmorillonite colloids.

The silica colloids have a pH of PZNPC of  $\sim 3.5$  (Langmuir, 1997). With a solution pH of  $\sim 8.2$  to  $8.4$ ,  $\text{SiOH}$  and  $\text{SiO}^-$  groups are the major surface functional groups on these colloids (Langmuir, 1997). Complexes of  $\equiv\text{SiO-Pu(OH)}_3^+$  and  $\equiv\text{SiO-Pu(OH)}_2^{2+}$  may thus be formed on the surfaces of silica colloids as well. It is unlikely that there are fixed charge sites on the amorphous silica colloids.

We observed that increasing temperature increased the adsorption of actinides by colloids. The species and oxidation states of actinides may be different in water at higher

temperatures. Also, most chemical reactions are faster at higher temperatures than at lower temperatures. Higher temperatures may also enhance the activity of surface sites.

We observed that increasing ionic strength decreased the adsorption of actinides by colloids. It is likely that at higher ionic strength, the cations, especially  $\text{Ca}^{2+}$  ions, strongly compete with actinides for surface sites. Also, increasing ionic strength may result in aggregation of colloids, lowering the total surface area available for adsorption. At higher ionic strengths ( $\geq 0.1$  M), the concentrations of  $\text{CaCl}_2$  were high enough to result in  $\text{CaCO}_3$  precipitation in the water, which apparently caused 100% of the  $^{238}\text{U}$  to co-precipitate at an ionic strength of 0.134 M.

## CONCLUSIONS

Our results show that colloids of hematite, montmorillonite, and silica sorbed more  $^{239}\text{Pu}$ ,  $^{243}\text{Am}$ ,  $^{237}\text{Np}$ , and  $^{238}\text{U}$  in the synthetic groundwater than in natural groundwater. Hematite colloids sorbed more of the actinides than montmorillonite or silica. Adsorption of  $^{239}\text{Pu}$  and  $^{243}\text{Am}$  was rapid, while adsorption of  $^{237}\text{Np}$  and  $^{238}\text{U}$  was a slow process. Temperature only slightly influenced the adsorption of  $^{239}\text{Pu}$  and  $^{243}\text{Am}$  by hematite and silica colloids, but it greatly affected the adsorption of  $^{239}\text{Pu}$  by montmorillonite colloids. Moreover, temperature also significantly influenced the adsorption of  $^{238}\text{U}$  and  $^{237}\text{Np}$  by all three types of colloids. While ionic strength did not influence the adsorption of  $^{239}\text{Pu}$  and  $^{243}\text{Am}$  by hematite colloids, increases in ionic strength decreased the adsorption of all four actinides onto montmorillonite and silica colloids. Uranium precipitation was observed in the solutions with higher ionic strengths ( $> 0.02$  M). Adsorption of  $^{239}\text{Pu}$  and  $^{243}\text{Am}$  per unit mass of colloid was much higher at the lower colloid concentrations than at the higher colloid concentrations. Desorption of  $^{239}\text{Pu}$  and  $^{243}\text{Am}$  from the three types of colloids was considerably slower than the adsorption process. However,  $^{237}\text{Np}$  and  $^{238}\text{U}$  did not desorb from any of the three types of

colloids in both natural and synthetic groundwaters. Instead, the residual radionuclides from the sorption process continued to be adsorbed slowly during the 212-day desorption period. Our results suggest that very little  $^{237}\text{Np}$  and  $^{238}\text{U}$  were adsorbed by colloids; these two actinides may transport primarily as dissolved species. On the other hand, strong adsorption and slow desorption of  $^{239}\text{Pu}$  and  $^{243}\text{Am}$  by colloids in groundwater may facilitate transport of radionuclides to the accessible environment along potential flowpaths from areas contaminated with radionuclides.

### ACKNOWLEDGMENTS

This research was funded by Yucca Mountain Program. We especially appreciate Phil Palmer for preparing the actinide stock solutions, Laura Wolfsberg for elemental analysis using ICP-MS and IC, Paul Reimus for technical review, and Wayne Lemons, and Jonathon Haradon for technical assistance.

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